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The recycling-oriented material characterization of hard disk drives with special emphasis on NdFeB magnets

Anna Dańczak [1], Ida Chojnacka [1], Sabina Matuska [1], Kamila Marcola [1], Anna Leśniewicz [1], Maja Wełna [1], Andrzej Żak [2], Zbigniew Adamski [1], Leszek Rycerz [1]

[1] Division of Analytical Chemistry and Analytical Metallurgy, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[2] Department of Materials Science, Strength and Welding Technology, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Corresponding author: anna.danczak@pwr.edu.pl (Anna Danczak)

Abstract: Hard disk drives (HDDs) consist of many components made from various materials: e.g. aluminum, steel, copper and rare earth elements (REEs). Recycling and reuse of these materials is desirable for economic and environmental reasons. Developing of potential HDDs recycling methods requires knowledge about HDDs material characteristic. The study aims to explore knowledge about structure and chemical composition of HDDs main components with special emphasis on NdFeB magnets. HDDs collected for the experiments came from Desktop PCs and Notebooks. The dependence between the average mass of HDDs components and such parameters as producer, year and country of production and disk capacity was analyzed. Chemical composition of NdFeB magnets and the heaviest components (i.e. top cover, mounting chassis, platters and metallic plates from magnet assembly of actuator) was analyzed by various analytical methods. The heaviest HDDs main components: top cover and mounting chassis, with the highest recycling potential, are made of aluminum and steel respectively. The majority of HDDs components showed also the existence of different alloy additions: C, Mg, Si, P, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sn and Pb. NdFeB magnets constitute 2.2 ± 1.1% of the average HDD from Desktop PC (517.3 ± 64.2 g) and 3.2 ± 1.2% from Notebook (108.2 ± 24.3 g). The chemical composition of NdFeB magnets from collected HDDs changes in the wide range: Fe (53–62%), Nd (25–29%), Pr (2–13%), Dy (0.1– 1.4%), Ni (2–6%), Co (0.5–3.6%), B (0.8–1.0%). Recycling of permanent magnets based on NdFeB alloys is potential remedy to fill the gap in the supply of rare earth elements on the global REEs market.

Keywords: *hard disk drives, rare earth elements, permanent magnets, recycling*

1. Introduction

Rare earth elements (REEs) are a group of 17 chemically similar metallic elements (15 lanthanides, scandium and yttrium). Nowadays they have become increasingly important, because of their essential role, among others, in permanent magnets, lamps and phosphors, catalysts and rechargeable batteries (Binnemans et al., 2013). The application of REEs has been changed in the last decade. Previous applications like metallurgy and ceramics have lost their significance and new applications such as permanent magnets, batteries, CCFL (Cold Cathode Fluorescent Lamps) and LED (Light-Emittiting Diode) phosphors have appeared (Goonan, 2011, Chancerel et al., 2015). In addition, rare earth elements are difficult to be replaced by other materials to obtain equivalent properties and appropriate electric or electronic components (Gutfleich et al., 2011). Usually only another rare-earth element can be used as a valuable substitute (Graedel et al., 2013).

The growing popularity of hybrid and electric cars, wind turbines and compact fluorescent lamps causes an increase in the demand and price of REEs. In 1996, the global mining of REEs was equal

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70,000 tons (Castor and Hendrick, 2006). The largest share in their application was in ceramic and glass industry, metallurgy and catalytic industry. In 2010, the global mining of REEs reached the value of 136,000 tons (Humphries, 2013) and it is increasing constantly.

Currently, China wields a near-monopoly over rare earth production: 50% of worldwide mineral reserves and 86% market share (Sprecher and Xiao et al., 2014). China's position as the largest producer of REEs seems to be unthreatened in the near future. Due to large and increasing domestic demands China tightened its REEs export from 50,145 tons in 2009 to only 31,130 tons in 2012 (Binnemans et al., 2013). Such limits in export of rare earths can cause serious problems for rare earths users outside of China. Many companies were forced to move the production of rare earths containing products to China in order to secure access to raw materials (Hurst, 2010). European Commission considers REEs as the most critical raw material group, with the highest supply risk (European Commission, 2010).

Lack of the local raw materials will force many countries to rely on recycling of REEs from pre-consumer scrap, industrial residues and REE-containing end-of-life products. This recycling can be a significant source of REEs and additionally it can solve so called "balance problem" (Binnemans et al., 2013; Sprecher et al., 2014). The demand and supply of individual rare earth elements should be equal. Otherwise, there will be a shortage or excess of some elements. REEs occur in minerals and ores in different ratios. For example, neodymium is much less common than lanthanum or cerium, so processing of these ores for neodymium produces also large oversupply of lanthanum and cerium. Recovering of neodymium from scraps would lead to reduction of REEs ores mining that needs to meet the global demand of this metal (Binnemans et al., 2013). In addition, recycling of REE-containing end-of-life products is less complex in comparison to processing of ores because the products directed into this process contain a smaller number of lanthanides (Ueberschaar and Rotter, 2014). Recycling can also help to avoid problems with radioactive thorium and uranium impurities in REE ores (Charewicz, 1990; IAEA Safety Report, 2011). The analysis performed by Simoni et al. showed that rare earth elements can be more environmentally friendly than primary production (Simoni et al., 2015). Despite these advantages, commercial recycling is still very low and less than 1% of rare earths are currently recycled (UNEP status report, 2011).

Nowadays, permanent magnets production is the application with the highest consumption of rare earth elements (Goonan, 2011; Chancerel et al., 2015). Two types of these magnets are produced: the neodymium-iron-boron and the samarium-cobalt magnets. According to European Commission about 13% of the worldwide mining output of neodymium is used for the manufacturing of permanent magnets (European Commission, 2010). Due to the neodymium magnets, superior magnetic flux density the neodymium-iron-boron magnets (NdFeB magnets) are the most widely used in hard disk drives (HDDs), stereo speakers, wind turbines generators and hybrid electric cars (Goonan, 2011). Magnets used in wind turbines and in hybrid and electric vehicles will be in service for long periods of time and, therefore, they are not currently available in large quantities in scrap today. At present the production of electronic goods (HDDs, loudspeakers, mobile phones) consumes the highest amount of permanent magnets (Du and Graedel, 2011; Oakdene Hollins, 2010). It is evident, that computer hard disk drives (HDDs) are the most important source of REEs scrap today (Chancerel et al., 2015). Du and Graedel estimated that in 2007 62,600 tons of neodymium and 15,700 tons of praseodymium, contained in permanent magnets, were stock in society (Du and Graedel, 2011). HDDs are used in computers, other Information Technology (IT) and Radio-Television (RTV) devices and also occur in the waste of used electrical and electronic equipment. Due to the rapid aging of electronic devices, both hard disks and the whole computers are often replaced with new equipment. Annual production of HDDs, which contain NdFeB magnets, is around 600 millions of pieces (Szalatkiewicz, 2010; Walton and Wiliams, 2011). Taking into account that the mass of NdFeB magnet in each HDD varies between 10 and 20 g, estimated mass of Nd-Fe-B alloy for recycling can reach 6,000 to 12,000 tons. Recycling of permanent magnets from HDDs seems to be a promising method of neodymium and other lanthanides recovery.

There are no current technologies for end-of-life recovery or rare earth magnets recycling (Öko-Institut, 2011). Numerous recycling processes have been reported (Bristøl, 2011). The variety of processes include molten salt processes (Oakdene Hollins, 2010), hydrometallurgical processes (Ellis et al., 1994), melt spinning (Itoh et al., 2004), glass slag method (Saito et al., 2003), slag electrorefining (Ellis et al., 1994), and extraction technologies using molten silver (Takeda et al., 2004) and magnesium (Ellis et al., 1994; Takeda et al., 2004, 2006; Oakdene Hollins, 2010;). Lately, the promising method of neodymium magnets recycling based on their decrepitation with hydrogen has been developed (Zakotnik et al., 2008, 2009; Walton and Williams, 2011; Harris et al., 2012). However, none of these methods has been commercially developed due to low yields, high costs and too low amounts of REEs in the waste. The investigations performed by Sprecher et al. showed that within the application of NdFeB magnets for HDDs, the potential for loop-closing is significant: up to 57% in 2017. However, Sprecher et al. concluded that compared to the total NdFeB production capacity, the recovery potential from HDDs is relatively small (in the 1–3% range) (Sprecher et al., 2014).

An efficient recycling process of the rare earth permanent magnets should be developed in the near future because of the effective use of rare earth resources. In addition, HDDs can be a potential source of various other valuable materials like aluminum, copper, steel which are easy to separate (Ueberschaar and Rotter, 2014). However, recycling of HDDs requires knowledge about material characterization of their particular components which has been proved by two research group (Ueberschaar and Rotter, 2014; Habib et al., 2014; Habib et al., 2015). Therefore, the aim of the research presented in this paper is to study chemical composition and structure of particular elements of HDDs and compare the obtained results with the literature data. The obtained results will be necessary in the future research on developing efficient method of HDDs recycling.

2. Materials and methods

2.1. Materials

Hard disk drives used in the experiments were obtained from different types of Desktop PCs (3.5" HDDs) and Notebooks (2.5" HDDs). The collected HDDs, in total number of 66 (47 from Desktop PCs and 19 from Notebooks), came from different producers, country and year of production and furthermore were characterized by different disk capacity. All of the HDDs were manual disassembled which is the crucial step for characterizing end-of-life devices to get information about structure and to separate components of interest of chemical analysis (Ueberschaar and Rotter, 2014).

The construction of different HDDs is very similar. The HDDs from Desktop PCs and from Notebooks are built of the same components. The difference occurs in the size and shape of individual components. Every hard disk contains: top cover, mounting chassis, electronics card, platter, spindle, read/write head equipped with arm, actuator, air filter and additional components like: ribbon cable, tape seal and screws (Figs. 1-2.). The number of platters is the biggest difference between the construction of hard disks (from 1 to 4).

In the present work, the special emphasis was put on the structure and chemical composition of NdFeB magnets. The magnet assembly of HDD actuators usually contains two NdFeB permanent magnets and each magnet is glued to one metallic plate (Fig. 3). In another, a less common case, only one permanent magnet is placed between two metallic plates.

Fig. 1. Hard disk from CONNER company: Particular elements: 1 – top cover; 2 – mounting chassis; 3 – electronics card; 4 – platter; 5 – spindle; 6 – read/write head; 7 – head arm, 8 – actuator

Fig. 2. Hard disks from SAMSUNG (A) and SEAGATE (B). Particular elements: 1 – top cover; 2 – mounting chassis; 3 – electronics card; 4 – platter; 5 – spindle; 6 – read/write head and head arm with ribbon cable, 7 – magnet assembly of actuator; 8 – screws, 9 – air filter

Fig. 3. The examples of magnets assembly of actuator from different hard disk drives (HDDs)

2.2. Methods

In present work, various methods were used to study the material characteristic of HDDs main components: top cover, mounting chassis, platters, permanent magnets and metallic plates from magnet assembly actuator.

The structure and material composition of magnets assembly of actuator can be analyzed only after separation of NdFeB magnets from metallic plates. Due to the generated magnetic fields and layer of glue keeping the magnets into position, sintered NdFeB magnets are difficult to separate from the metal plates. The solution for their separation is demagnetization. This process can be executed by applying a strong magnetic field opposite to the original magnetization direction or heating a magnet above the Curie temperature. In the present work, the second method was used. The Curie temperature of NdFeB alloys was estimated at 585 K (Leonowicz and Wyslocki, 2005; Paszkowski, 2008). In our work the process of demagnetization was conducted at 623 K. During demagnetization the all magnets were separated from the metal plates.

2.2.1. Mass analysis of the HDDs main components

The weight of the HDDs main components is necessary in pursuing chemical analyses for an estimation of the overall share of focused materials (Ueberschaar and Rotter, 2014). In order to verify the dependence between mass of individual elements and such parameters as: hard disk capacity, date and country of production and also the hard disk producer, the all of the 70 HDDs were examined. The collected HDDs were weighed and after manual disassembly the individual components were divided into 10 groups and also weighed separately.

2.2.2. Quantitative analysis of NdFeB magnets

Quantitative analysis of NdFeB magnets from HDDs was conducted following by X-ray powder diffraction method (XRD). For this purpose, measurements in the symmetric $\theta/2\theta$ Bragg-Brentano geometry using Philips X'PERT system were performed. The device was equipped with a PW 1830 generator, PW 3710 control module and PW 3719 counter. CuKα radiation, vertical goniometer, angle and position reflexes registration counters were applied. Measuring range of the 2 theta angle was 3-100° step – 0.05°, a single pulse counting time – 2 seconds, voltage – 40 kV, current – 30 mA. Treatment of experimental data was carried out using software DHN-Powder Diffraction System. Identification of different phases of NdFeB magnets was carried out by comparison of the experimental powder diffraction patterns of the sample with reference patterns stored in the Powder Diffraction Files database (International Centre for Diffraction Data PDF-2 base).

In addition the microstructure of NdFeB magnets was analyzed using optical microscope Nokon Eclipce MA200 with CCD Nikon Ds.-F1 camera.

2.2.3. Elemental composition of NdFeB magnets

NdFeB magnets as each material applied in electric and electronic equipment (EEE) is embedded in specific matrix related to its functional use. It is well known that matrix had significant influence on the quality of results (Ueberschaar and Rotter, 2014). Therefore, the developing of calibrations using standard samples with the same matrix as the samples and with known concentration of elements which have to be determined is necessary (Chancerel and Rotter, 2009). In our study an ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) was applied to achieve the most accurate results.

The first evaluations of NdFeB magnets chemical composition were performed following EDS (Energy Dispersive Spectroscopy) method. This technique is intended to obtain a second set of comparable results of magnets elemental composition. The fragments of three randomly chosen NdFeB magnets (characterized by different size and shape) were hot mounted in a phenolic formaldehyde resin at temperature 440 K under the pressure of 6 MPa. Subsequently, a metallographic section was prepared. Chemical composition of the prepared samples was studied with a Scanning Electron Microscope JEOL JSM-6610A with a JED-2300 EDS (Si-Li type, Mini-cup). Tungsten filament and accelerating voltage 20kV were used. The samples were not covered with any additional layers and electrical conductivity was provided by copper tape. Quantitative analysis was performed using ZAF method which is the correction method of three effects: the atomic-number effect, the absorption effect, fluorescence excitation effect.

The chemical analyses performed by ICP-OES method were carried out for a broad range of elements to obtain high detection range. Following elements were measured: B, Co, Fe, Ni, Dy, Tb, Nd and Pr.

The ICP-OES method was used in the study of NdFeB magnets chemical composition also by Ueberschaar and Rotter. In their work the samples of the actuators have been crushed and subsequently milled in an agate vibrating tube mill. The acidulation was conducted with 300 mg sample material and 6.66 cm^3 of ultrapure water and 3.33 cm^3 of HNO_3 solution (Uberschaar and Rotter, 2014). In this work, different approach was applied. The first step of investigations was the demagnetization of magnet assembly of actuator. NdFeB magnets were separated from the metallic plates. Prior to the analysis, the classical wet mineralization using *aqua regia* (mixture of 65% HNO_3 and 37% HCl with volume ratio: 3:1) was used for dissolution of NdFeB magnets. The magnets were weighed on analytical balance with accuracy ±0.0001 g and transferred into glass beakers. Then *aqua regia* solution was added and reaction of dissolution was continued during 24 hours (to conduct preliminary mineralization). After this time, the samples in the beakers were heated on a hot-plate and the further portions of *aqua regia* were added until achieving clear solutions. The cooled solutions were transferred quantitatively into volumetric flasks and completed with redistilled water to a convenient volume. Before the spectrometric measurements, the sample solutions were suitably diluted. Procedural blanks were also prepared in the same way as the samples, in order to make correction of analytical signals.

Concentrations of the elements were determined using an optical Jobin Yvon (France) sequential ICP-OES instrument (JY 38S) equipped with monochromator with a 1 m focal length and double holographic grating (4320 and 2400 lines/mm). Operating parameters were as follows: the RF power 1000 W; the plasma observation zone radial, 12 mm above load coil; the plasma gas flow rate: 13.0

$dm^3 \cdot min^{-1}$; the auxiliary gas flow rate: 0.2 $dm^3 \cdot min^{-1}$; the nebulizer gas flow rate: 0.38 $dm^3 \cdot min^{-1}$; the sample flow rate: 0.75 $cm^3 \cdot min^{-1}$; the integration time: 0.1 s. The sample solutions were introduced into the plasma by using a parallel Burgener-type pneumatic nebulizer and a single-pass glass cyclonic spray chamber. Analytical lines of B (249.8 nm), Co (228.6 nm); Dy (353.2 nm); Fe (259.9 nm); Nd (401.2 nm); Ni (221.6 nm); Pr (414.3 nm) and Tb (350.9 nm) were measured. The type-curve method was used as a calibration method. The standard solutions of B, Co, Fe and Ni were prepared by dilution of commercial multi-elemental solution (Merck, 1000 mg/dm^3). The multi-elemental standard solutions of Dy, Nd, Tb and Pr were prepared from commercial one-elemental solutions (Merck 1000 mg/dm^3). The concentration of standard solutions used for calibration covered the range 0–5.0 mg/dm^3.

2.2.4. Chemical composition of HDDs main components

In the present work only the main HDDs components with the highest recycling potential were investigated: top cover, mounting chassis, platters and metallic plates from magnet assembly of actuator. Determination of chemical composition of HDD main components was carried out with EDS method using a CCD-Based Glow Discharge Atomic Emission Spectrometer (Leco Company). The device was calibrated for analyzing Fe and Al alloys. The accelerating voltage of electron gun was 20kV. Samples of investigated components were prepared in the same way as samples of NdFeB magnets for the same measurements method. The analysis of upper cover and platter were conducted after grinding of outer layer of samples on sandpapers grit 120 and 320. Determination of chemical composition of mounting chassis and solid cover was carried out on the cross-section of the sample, after grinding. A broad range of following elements was measured: Si, Mg, Fe, Cu, Sn, Zn, Cr, Ni, Mn, Pb, Al, Ti, C, P, and V.

3. Results and discussion

HDDs can be a valuable source not only of REEs, but also of other metals. Therefore, identification of composition of HDDs components is important for further recycling process. In present work NdFeB magnets and the heaviest components (i.e. top cover, mounting chassis, platters and metallic plates from magnet assembly of actuator) were analyzed.

3.1. Mass analysis of the HDDs main components

Absolute weight of HDD from Desktop PC (3.5″ HDD) is 517.3 ± 64.2 g and of HDD from Notebook (2.5″ HDD) is 108.2 ± 24.3 g. The average weight of HDDs main components is showed in the Table 1.

Table 1. The average mass (g) of HDDs components

	The average mass (g)	
	3,5" HDD	2,5" HDD
Total mass	517.3 ± 64.2	108.2 ± 24.3
Top cover	111.6 ± 40.4	12.6 ± 5.3
Mounting chassis	242.0 ± 46.1	56.2 ± 7.2
Electronics card	41.3 ± 19.3	12.8 ± 2.6
Platters	31.0 ± 15.5	8.4 ± 4.2
Platter's mounting	5.9 ± 2.9	3.5 ± 1.2
Spindle	53.3 ± 14.6	
Read/write head with the arm	18.9 ± 5.9	
Screws	7.2 ± 1.7	2.0 ± 1.0
Magnet assembly of actuator	48.6 ± 21.9	12.6 ± 5.8
Remainings	2.6 ± 2.2	5.5 ± 4.5

The dependence between mass of different HDDs components and such parameters as: hard disk capacity, year and country of production and also the hard disk producer was estimated. The results for the heaviest HDDs components are shown in Tables 2-4. As can be seen from the tables, the weight of particular components is not related to the capacity, year of production and producer of a hard disc. The biggest difference between the constructions of HDDs is the number of platters, however this number is not related to HDDs capacity, year of production and the producer.

The voice-coil actuator has a share of 9.9 ± 3.3% of an average 3.5″ HDD and 11.4 ± 3.1% of and average 2.5″ HDD. Usually HDDs actuator contains two permanent magnets glued to the metallic plates (Fig. 3). After the demagnetization process NdFeB magnets were weighted. The average mass of magnets in one Desktop PC HDD fluctuates from 6 to 19 g and in one Notebook HDD from 2 to 6 g (Fig. 4). The results showed also that the mass of magnets is not related to the capacity, a year of production and the producer of a hard disk (Figs. 4-6).

Table 2. The average mass (g) of the 3.5″ HDD components from different producers

Producer	Total mass	Top cover	Electronics card	Platters	Mounting chassis	Spindle	Magnet assembly of actuator
CONNER	504.3 ± 1.3	100.9 ± 10.0	73.6 ± 13.1	33.96 ± 15.22	146.6 ± 24.5	52.1 ± 16.2	50.0 ± 20.1
HITACHI	545.3 ± 10.1	182.5 ± 6.3	23.1 ± 0.9	23.1 ± 0.9	250.4 ± 0.6		42.7 ± 0.1
IBM	538.5 ± 10.8	87.2 ± 11.0	50.7 ± 22.2	29.9 ± 12.1	178.9 ± 32.8	83.8 ± 32.7	64.5 ± 19.3
MAXTOR	524.7 ± 21.4	119.3 ± 25.4	29.6 ± 3.9	22.0 ± 2.1	261.9 ± 26.5	35.3 ± 0.1	25.1 ± 1.9
SAMSUNG	544.4 ± 68.1	161.2 ± 31.8	33.5 ± 2.5	24.9 ± 8.9	191.2 ± 19.1	47.3 ± 4.4	58.3 ± 29.5
SEAGATE	537.1 ± 83.9	87.8 ± 22.3	38.5 ± 26.6	40.5 ± 23.2	234.2 ± 46.0	60.2 ± 3.4	43.9 ± 19.7
QUANTUM	492.7 ± 5.5	118.7 ± 0.9	42.3 ± 2.7	22.1 ± 10.4	193.6 ± 1.8		59.7 ± 8.3
VIRAGO	524.9 ± 1.5	112.5 ± 1.2	57.6 ± 1.6	44.2 ± 1.3	129.0 ± 0.6	59.3 ± 0.1	83.2 ± 0.1
WESTERN DIGITAL	469.6 ±60.3	90.4 ± 36.7	49.1 ± 15.3	33.0 ± 15.1	165.9 ± 43.9	48.9 ± 4.1	51.5 ± 21.5

Table 3. The average mass (g) of the 3.5″ HDD components obtained from HDDs of different capacity

Capacity	Total mass	Top cover	Electronics card	Platters	Mounting chassis	Spindle	Magnet assembly of actuator
Less than 1 GB	495.0 ± 26.1	100.4 ± 23.7	65.9 ± 7.9	36.5 ± 13.7	138.4 ± 21.5	48.4 ±9.5	63.4 ± 20.5
10-30 GB	528.2 ± 9.8	127.8 ± 7.6	33.5 ± 2.9	26.0 ± 3.8	192.1 ± 14.6	46.5 ±12.4	61.3 ± 17.3
40 GB	522.7 ± 21.8	114.9 ±12.4	28.5 ± 13,8	23.3 ± 2.6	241.7 ± 12.9	49.8 ± 10.5	37.0 ± 3.7
60 GB	494.6 ± 22.1	91.7 ± 11.2	33.6 ± 12.7	34.5 ± 13.5	209.1 ± 10.8	50.6 ±7.3	44.0 ± 26.1
80 GB	505.1 ± 3.6	120.0 ± 6.8	29.7 ± 10.7	23.9 ± 9.0	229.3 ± 2.8	18.2 ± 1.0	50.2 ± 8.7
120-160 GB	561.8 ± 2.7	128.5 ± 7.9	29.5 ± 4.7	40.9 ± 3.8	226.4 ± 6.5	55.5 ±15.3	41.7 ± 10.6
More than 250 GB	619.5 ± 21.9	112.3 ± 21.9	20.3 ± 1.7	80.0 ± 4.0	254.0 ±16.8	30.0 ±6.3	71.6 ± 22.3

Table 4. The average mass (g) of the 3.5″ HDD components obtained from HHDs of a different year of production

Year of productio n	Total mass	Top cover	Electronics card	Platters	Mounting chassis	Spindle	Magnet assembly of actuator
1991-1995	471.4 ± 20.3	94.6 ± 13.6	47.2 ± 11.2	28.7 ± 7.5	161.7 ± 16.5	47.5 ± 9.3	54.6 ± 23.4
1996-2000	509.5 ± 42.1	147.1 ± 26.7	66.4 ± 25.9	37.8 ± 8.1	102.3 ± 24.8	47.3 ± 4.6	64.7 ± 17.3
2001-2005	528.1 ± 17.4	139.1 ± 4.6	31.4 ± 9.4	27.5 ± 3.7	207.2 ± 22.8	46.7 ± 10.5	47.1 ± 20.7
2006-2010	527.2 ± 24.6	142.8 ± 22.5	29.2 ± 16.8	25.0 ± 2.0	209.0 ± 15.8	50.9 ± 11.6	40.5 ± 12.4

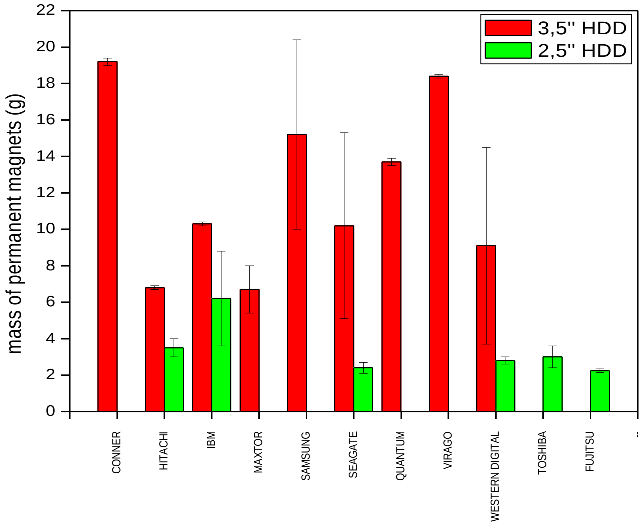

Fig. 4. The average mass (g) of the permanent magnets and from the HDDs from different producers

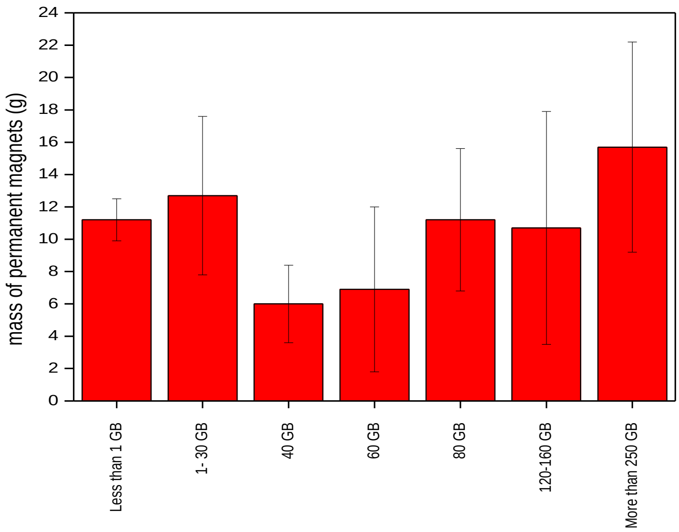

Fig. 5. The average mass (g) of the permanent from 3.5″ HDDs characterized by different disk capacity

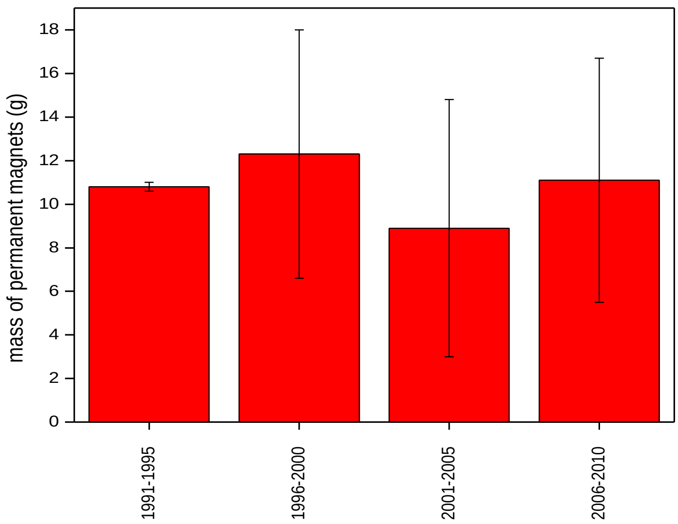

Fig. 6. The average mass (g) of the permanent magnets from 3.5″ HDDs characterized by different year of production

3.2. Quantitative analysis of NdFeB magnets

The investigation of quantitative composition of NdFeB magnets from HDDs were conducted using XRD measurements. The XRD patterns of the magnets recorded in the 2θ range from 3 to 100° are shown in Fig. 7. Analysis of the experimental diffraction patterns allows to state that metallic nickel covers the magnets surface. XRD pattern is similar to that of the metallic nickel standard card number 04-0850. The peaks positions are similar to corresponding ones in the standard pattern. Also, the relative intensities of the experimental peaks are comparable to those given in the standard. The characteristic peaks appearing at 2θ = 44.51°, 51.85°, 76.37°, 92.94°, 98.45° prove the presence of metallic nickel on the magnets surface.

XRD pattern were also recorded for powdered NdFeB magnet after Ni layer removing. It is presented in Fig. 8. Compatibility of the peaks positions between experimental pattern achieved for powdered magnets and the standard cards numbered: 36-01296 and 39-0473 proved the presence of $Nd_2Fe_{14}B$ phase in the analysed sample.

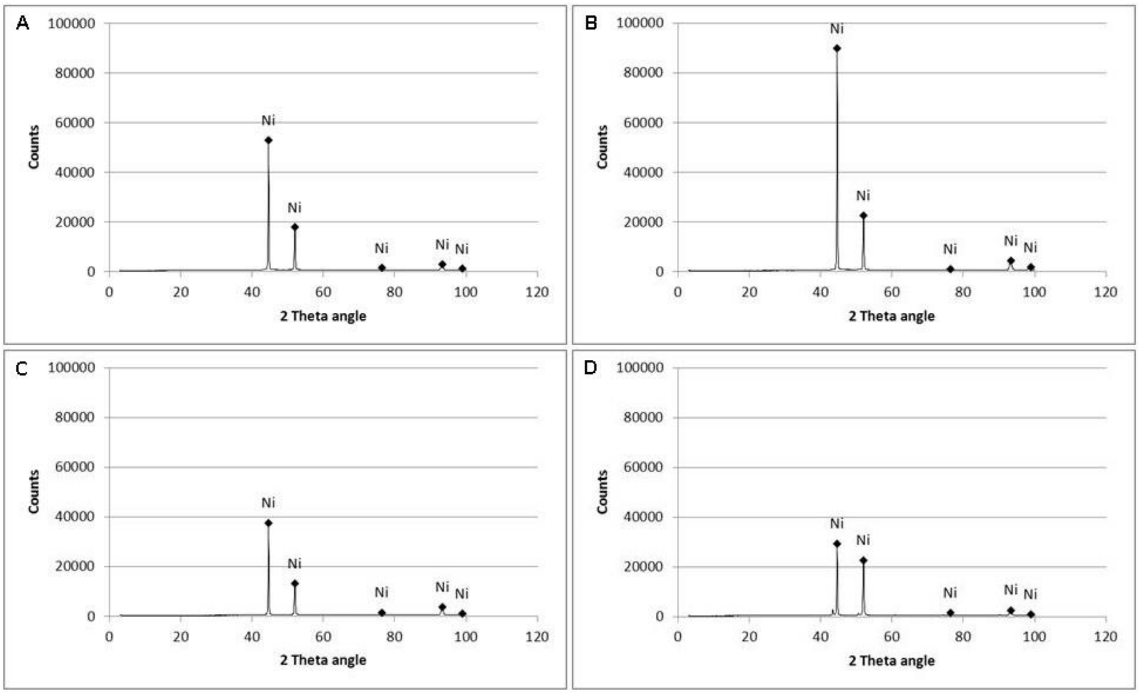

Fig. 7. XRD pattern of (A) magnet no. 1; (B) magnet no. 2; (C) magnet no. 3; (D) magnet no. 4

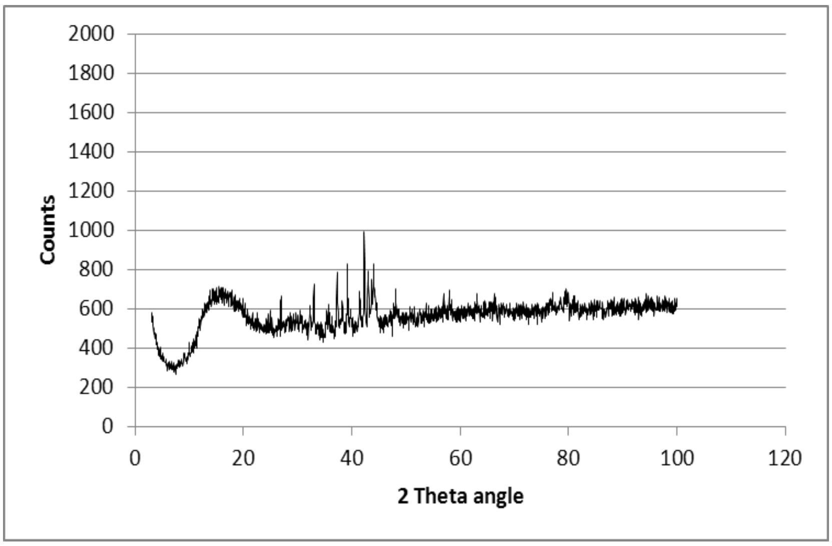

Fig. 8. XRD pattern of powdered NdFeB magnet

The photographs of the microstructure of NdFeB magnets and metal plate are shown in Fig. 9. The magnets based on NdFeB alloys are characterized by porosity of the native material and by a weak connection between outer layer and the core.

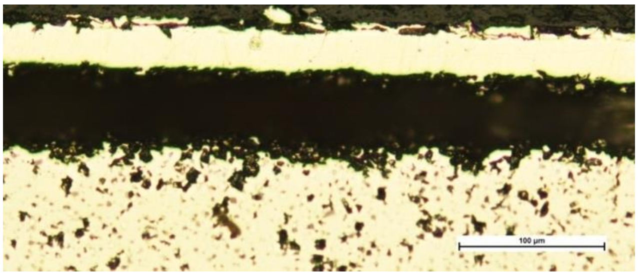

Fig. 9. Microstructure of NdFeB magnet

3.3. Chemical composition of NdFeB magnets

The chemical composition of NdFeB magnets was determined by two different analytical methods (EDS and ICP-OES) in order to obtain comparable results. The first step was the determination of the chemical composition by EDS method. Three NdFeB magnets from varied HDDs characterized by different size and shape were investigated. The core of magnets is composed of 71.38% ± 1.81% of Fe and of 25.15% ± 2.34% Nd and in two cases also of about 5% Pr. The cores of magnets are coated with a thin layer of Ni (99.77% ± 0.05%).

The chemical analysis by ICP-OES method was conducted for four magnets (characterized by different size and shape) from varied HDDs. According to the experimental data presented in Table 6 the composition of magnets is not uniform and is changing in relatively wide range: Fe (53–62 %), Nd (25– 29%), Pr (2–13%), Dy (0.1–1.4%), Ni (2–6%), Co (0.5–3.6%) and B (0.8–1.0%).

Table 5. The results of NdFeB magnets chemical composition determination by EDS detector

	Magnet no. 1		Magnet no. 2		Magnet no. 3	
Element of composition	outer layer	core	outer layer	core	outer layer	core
Ni%	100.00 ± 0.50		100.00 ± 0.48		99.13 ± 0.51	
Fe%		69.65 ± 0.51		71.57 ± 0.49	0.87 ± 0.43	72.93 ± 0.45
Nd%		25.04 ± 0.93		23.33 ± 0.90		27.07 ± 0.83
Pr%		5.31 ± 0.85		5.10 ± 0.91		
Others						indication of Dy

Table 6. The results of chemical analysis of NdFeB magnets (values in weight %)

No. of sample	B	Fe	Ni	Dy	Nd	Pr	Co
1	0.867 ± 0.019	53.3 ± 0.3	3.37 ± 0.10	1.42 ± 0.04	28.7 ± 0.6	2.05 ± 0.09	3.61 ± 0.05
2	0.871 ± 0.040	61.9 ± 0.1	1.92 ± 0.06	0.818 ± 0.003	26.4 ± 0.2	11.3 ± 0.2	0.540 ± 0.025
3	0.848 ± 0.009	55.3 ± 0.6	6.38 ± 0.03	1.33 ± 0.09	24.9 ± 0.8	12.8 ± 0.2	0.486 ± 0.008
4	0.959 ± 0.056	55.2 ± 0.2	2.79 ± 0.02	0.080 ± 0.002	26.2 ± 0.2	11.3 ± 0.5	1.01 ± 0.07

3.4. Chemical composition of HDDs main components

The following components of HDDs were selected for material composition analysis: top cover, mounting chassis, platters and metallic plates from magnets assembly of actuator. Composition of the HDD top cover and mounting chassis was determined using a spark discharge optical spectrometer.

Based on results presented in Figs. 10-11 the building material of the mounting chassis was identified as an Al-Si alloy. The top cover is made of steel with a high content of Cr. The presence of this element suggests that it is built of ferritic steel 1.4016 (according to standard PN-EN 10088). However, the excess of such an element as P is not compatible with the same standard.

The analysis of EDS spectra of the platter's core and outer layer allowed to determine the quantitative composition of the platter core and outer layer 94.87% ± 0.42% of Al, 5.13% ± 0.38% of Mg, 87.36% ± 0.55% of Ni and 12.64% ± 0.92% of P, respectively. This suggests that the platter's core is based on EN-AC-AlMg5 alloys (according to standard PN-EN 1706:2001).

The metallic plates from magnet assembly actuator were investigated after separation from NdFeB magnets. In comparison to the magnets the chemical composition of metallic plate is completely different. The core is composed only of Fe and the outer layer contains Ni (87.75% ± 0.54%), Fe (1.76% ± 0.48%) and P (11.49% ± 1.03%).

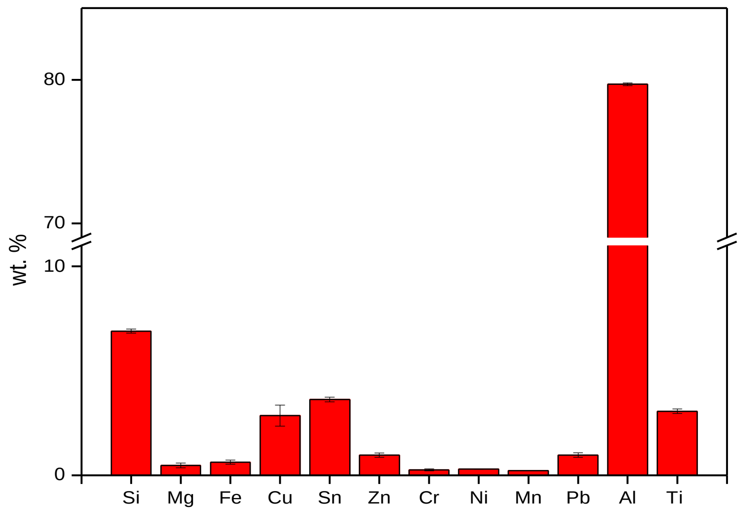

Fig. 10. Chemical composition of the HDD mounting chassis

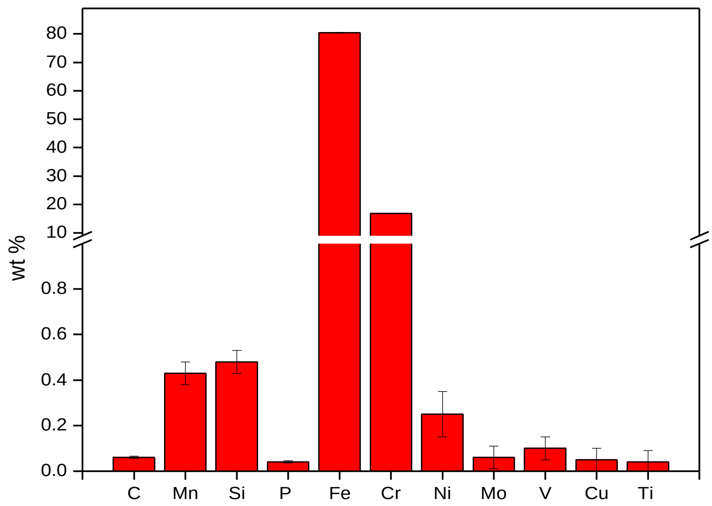

Fig. 11. Composition of the HDD top cover

4. Discussion

Information about material characterization of hard disk drives (HDDs) is required for developing efficient HDDs recycling method. Several studies have focused on material characterization of HDDs components (Ueberschaar and Rotter, 2014; Habib et al., 2014, 2015). Ueberschaar and Rotter studied structure and composition of analysis of HDDs from Desktop PCs and Notebooks which were disassembled in two German pretreatment recycling plants. For the determination of the product structure and material composition the researchers used the quantitative and semi-quantitive analytical methods: ICP-OES, ICP-MS and X-Ray fluorescence analysis (Ueberschaar and Rotter, 2014). Habib K. et al. performed the study on chemical composition analysis of HDDs components and material flow analysis of HDDs. Samples of HDDs (from Desktop PCs and from Notebooks) were collected randomly from waste electrical and electronic equipment (WEEE) treatment plant in Denmark. The chemical composition of particular components was analyzed using X-ray fluorescence (XRF) spectroscopy method (Habib et al., 2015).

The results obtained by Habib et al. (2015) demonstrated the complete loss of rare earths in the existing shredding-based waste electrical and electronic equipment (WEEE) treatment processes. Furthermore, dismantling and separate processing of NdFeB magnets from their end-use products can be more preferred option over shredding (Habib et al., 2015).

According to Uebershaar and Rotter (2014) HDDs are made mostly from non-ferrous materials 67%, in which the main element is aluminum 96-98%. Habib et al. (2015) confirmed that Al is the dominant constituent of both types of HDDs (50% weight of 3.5″ HDDs and 40% of 2.5″ HDDs). In this work, the results showed that the heaviest HDDs main components: top cover and mounting chassis, with the highest recycling potential, are made of steel and aluminum respectively. The majority of HDDs components showed also the existence of different alloy additions: C, Mg, Si, P, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sn and Pb which recovery potential should be studied also in future.

NdFeB magnets are a part of the HDDs actuators which show a share of 48.6 ± 21.9% of an average 3.5″ HDD and 12.6 ± 5.8% of an average 2.5″ HDD. Demagnetization process following by heating above Curie temperature was required for separation of magnets from metallic plates and for analyzing the magnets chemical structure. The possibility of using the complete magnets assembly of actuator in REEs recovery process, without separation of magnets, should be examined.

The results showed that NdFeB magnets constitute 2.2 ± 1.1% of 3.5″ HDD and 3.2 ± 1.2% of 2.5″ HDD which is in good agreement with the literature data: 3 ± 1.5% and 2.2 ± 1.0% for 3.5 HDD and 5.8 ± 0.7%, 2.9 ± 0.5% for 2.5″ HDD (Ueberschaar and Rotter, 2014; Habib et al., 2014). Determined chemical composition of NdFeB magnets consists of Fe, B, Co, Ni and rare earth elements: Nd, Pr and Dy. The weight percentage of different elements in the NdFeB magnets changes in the wide range and it does not depend of the size and shape of magnets and of HDDs producer. For this reason, we suggest that the universal recycling method should be developed for all NdFeB magnets regardless of magnets chemical composition.

Hard disk drives (HDDs) can be potential source of many valuable elements: rare earth elements (mostly neodymium), Fe, Al, Cr, Ni and Cu. However, dismantling and separate processing of HDDs components remains as technological and logistic challenge in the recycling process. The results obtained in this work and also the results from Ueberschaar and Habib (Ueberschaar and Rotter, 2014; Habib et al., 2014) proved that HDDs are characterized by complicated structure and thereby a difficult access to the NdFeB magnets. An efficient recycling process of the NdFeB magnets should be developed in the near future due to the growing demand of rare earth resources.

5. Conclusions

Hard disk drives (HDDs) components are made from various materials which are potential source of many valuable elements e.g. Al, Fe, Cu and rare earth elements (REEs). This study showed that HDDs from Desktop PCs and from Notebooks consist of the same components, which weight does not depend on the producer, year or country of production and disk capacity. The heaviest HDDs components are made of aluminum and steel and also showed the existence of different alloy additions: C, Mg, Si, P, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sn, Pb. NdFeB magnets, which are a part of HDDs actuators, are potential source of rare earth elements (mostly neodymium and in smaller amount praseodymium and dysprosium). The chemical composition of NdFeB magnets changes in the wide range and does not depend on the HDDs parameters. A universal recycling method for all NdFeB magnets from HDDs, regardless of the chemical composition, should be develop in the industrial scale in the near future.

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