

氏名	ひさのせいいち 久野誠一
授与学位	博士(学術)
学位記番号	学術(環)博第37号
学位授与年月日	平成17年9月6日
学位授与の根拠法規	学位規則第4条第1項
研究科, 専攻の名称	東北大学大学院環境科学研究科(博士課程)環境科学専攻
学位論文題目	金属系高密度磁気記録材料の開発
指導教官	東北大学教授 田路 和幸
論文審査委員	主査 東北大学教授 山崎 仲道 東北大学教授 粕谷 厚生 (工学研究科)
	東北大学教授 村松 淳司(工学研究科)
	東北大学助教授 バラチャンドラン ジャデワン

論文内容要旨

Abstract

Development of metallic magnetic materials for recording media

Transmission, storage and utilization of information play a vital role in the modern world. Thus the author aimed at developing materials for magnetic recording media, which supported the audiovisual, communication and information areas and any advancement is expected to bring considerable progress. The author developed a technique to produce Fe_2O_3 powder for magnetic recording, by utilizing the knowledge acquired in magnetic material synthesis through the preparation of ferrite, crystal growth techniques through the synthesis of ZnO crystals and inhibition of sintering in pigments. And also, the experience gained in handling gas, heat, construction and operation, and other core techniques required for the development of magnetic recording media such as, product design, development requisites, mass production and product evaluation.

The magnetic recording density is increasing by approximately 2dB per year. This is being realized through the shortening of the wavelength, which was made possible only through the enhancement in the properties of the magnetic material such as coercivity(H_c) and remanence (B_r) rather than the recording width. The H_c increased by 10 fold from 250 to 2500 Oe and B_r by 4.5 fold from 1000 to 4500 G when the recording material was switched over from $\gamma\text{-Fe}_2\text{O}_3$ to the recently developed alloy of Co. In addition to the basic requirements such as high output and low noise, many other properties such as reliability, stability, long-term storage and matching with hardware are essential. One of the important factors affecting the magnetic properties of the recording materials is their magnetocrystalline anisotropy. Though the origin of magnetic anisotropy are shape and crystallinity of the material, shape anisotropy is being utilized in the

cases of γ -Fe₂O₃ and metal powders by making the grains acicular in shape. In the future, if the size of the magnetic grains is to be reduced to attain high recording density, retaining the shape could be difficult and so the shape anisotropy. And also, the crystalline anisotropy could become very sensitive to temperature and affect the practical application of the magnetic material. Though metallic magnetic recording material has the intrinsic advantages of high saturation magnetization (σ_s) and coercivity (H_c) depending on their magnetic constituents over the oxide counterpart, reactivity and dispersability during preparation and durability and degradation during practical use are considered detrimental. After reviewing the advantages and disadvantages of each processes, the author concluded that the synthesis of magnetic recording material using FeOOH as the starting material was superior to others when mass production, and shape control are considered.

Aging time during the neutralization process significantly affect the morphology of the goethite (FeOOH). As the aging time becomes longer, particles become finer. Consequently, the surface area of the powder and the branching of the crystal increases. When the morphology of the goethite is monitored during neutralization, we could find that hexagonal plate-like iron hydroxide is formed initially. Then, when the iron hydroxide is further oxidized, the formation of goethite begins near the edges of the plate and branches off at an angle of 60 degree. Finely dispersed hydroxide particles could be obtained by reverse neutralization within a short time under supersaturated condition. Metal particles with excellent switching field distribution (SFD) and OR were produced by reducing the above material. If the neutralization temperature is higher, the number of branches increase and the SFD, SQx and OR of the powder deteriorates. Al doped goethite could be produced by adding Al during neutralization of the solution with pH not less than 12. Compared with goethite, the lattice constant of the Al doped goethite was smaller and suggested that the Al is substituted for Fe in goethite.

Al doped goethite has a higher decomposition temperature than the Al-free goethite. Since the Al doped goethite retains its shape and inhibits sintering, it exhibited good dispersible and orientation properties. However, the non-magnetic layer thickness increases with increasing concentration of Al and leads to the decrease in saturation magnetization. Furthermore, excessive addition of Al causes pores in the particles and consequently the coercivity is reduced. Al doped powder that withstands degradation consists of metal particles with pores and different crystal orientation, surrounded by spinel structured oxide layer containing Al and Fe that acts as oxygen barrier and Al, Fe composite oxide layer that inhibits sintering.

For higher recording density, development of ultrafine metal powder with high H_c and B_r is indispensable. Ultrafine metal powders synthesized using the conventional process exhibited low H_c , and σ_s . In addition, they were unstable in oxidizing atmosphere and possess low durability. These problems were solved by making the particles acicular in shape, alloying with Fe-Co and doping with Y to inhibit sintering. Even particles that were 0.1 μ m in length could be made acicular in shape, dispersible and possess orientation property by doping with Y and Al. Fe-Co alloying improved the magnetic properties such as, H_c , σ_s and durability. Furthermore, the addition of Co prevented the coarsening of the crystals and high output and low noise was realized. However, when the length of the major axis was less than 0.1 μ m, the coercivity dropped drastically. Especially, when the axial ratio of the particle becomes less than 5, particles with H_c

less than 2 kOe increased remarkably. To obtain ultrafine particles, the axial ratio of the iron hydroxide that undergoes reduction has to be decreased. As a consequence, it is necessary to take steps to prevent them from sintering. In the improved metal powder, the oxide layer has become a few nanometers thick; number of pores reduced and the particles became almost single crystal. The concentration of Co was found to increase from the surface to center of the particle. It is believed that most of Y accompanied Al and remained at the surface of the particle forming Fe, Co complex oxide. Improved metal powder particles could be synthesized with H_c greater than 2 kOe. However the H_c decreased, when the particles diameter was reduced further. Although the saturation magnetization, σ_s was improved, it is still less than the bulk value of 240 emu/g and there is hope for further improvement.

Fct-FePt particle with diameters ranging between 7 and 10 nm was synthesized reacting iron and platinum acetylacetonate at 300 °C by using the polyol process. However, remarkable improvement of H_c could not be observed, as the particles were polycrystalline in nature. Thus, the synthesis of FePt particles using H_2PtCl_6 as nucleating agent and carboxylic acid as complex agent facilitated the formation of single crystal FePt nanoparticle with enhanced magnetic properties. fct-FePt nanoparticles with optimum magnetic properties was obtained by the addition of 1 at.% H_2PtCl_6 and 5 equivalent of Carboxylic acid. The Fe:Pt ratio was 52.5:47.5.

In the beginning, 230 nm size metal powders were realized for practical use by researchers. Although it was mentioned in the literature that the magnetic properties deteriorates when the particle size becomes less than 100 nm, 45 nm metal powder was realized with better magnetic properties. The H_c was increased from 1.5 to 2.5 kOe, and σ_s , σ_r and $\Delta\sigma_s$ were also improved or maintained. The success in the development of excellent metal powders depended on the design of the original composition, process, equipment, estimation and control. The metal powder developed was very simple in composition with the elements of Fe, Al, Ni and O compared with the conventional metal powder, which was composed of about 10 elements. In order to achieve improved properties with simple composition, the physico-chemical factors such as, equipment and control were important. For example, an original equipment (plant) that could supply H_2 , maintain low H_2O content that facilitated increased reaction rate by quickly removing H_2O during reduction was developed. Though the improvement in H_c was maintained even with the reduction in particle size, the magnetization continued to decrease as surface area and the volumetric ratio between the non-magnetic and magnetic phases increased. And also, the anisotropy decreased with the lowering of the melting point. Furthermore, improvement is necessary in reducing non-magnetic and superparamagnetic fraction. As many high potential materials are to be identified, there are possibilities for a breakthrough in magnetic recording material. Although FePt is not a new material, it has become a potential material for recording application with the advances in polyol process.

論文審査結果の要旨

本論文は、少エネルギー、少資源の21世紀の主角を担う、磁気記録メディアに要求される、高信頼性かつ高密度記録密度を達成できる素材の開発を環境科学の観点を踏まえて実施した研究成果である。磁気記録の歴史の中で、記録媒体として実用化されている素材は、酸化物系が中心となっていた。その大きな理由は、記録状態の経時変化の少ない、すなわち記録能力ではなく、長期間の情報保持に優れているという特徴が優先され利用されてきた。このことは、次世代の記録媒体としては、記録能力、すなわち金属系微粒子で安定な微粒子が理想とされていた。本研究は、このような要求を満足する金属系かつ長期にわたって安定な磁性微粒子の開発から今後の1テラビットという記録密度を達成するための金属系磁性微粒子の開発を目的とした研究であり、全編5章からなる。

1章は、緒論であり、本研究の意義と目的を記録媒体として利用できる磁性粉の開発の歴史と動向も踏まえて詳細に述べている。さらに、開発のブレークスルーとなる基礎技術と独創性を生むきっかけとなった要素技術についても詳細に述べられている。

2章では、金属磁性微粒子の安定性を確保するために、これまで固溶が困難とされていたアルミニウムを固溶させるための基本技術開発、さらび磁気記録特性を向上させるための微粒子サイズ分布の制御技術、さらに実用化で重要となる磁性微粒子の表面処理技術の開発などについて詳細な実験を行っている。その結果、温度60度、相対湿度90%という悪条件においても、1週間経過した時点での劣化率が20%以下と言う従来にないアルミニウム固溶鉄金属磁性微粒子を開発した。さらに、調製した微粒子について機器分析を用いてアルミニウムの固溶状態、さらに微粒子の構造および形態に関する詳細なキャラクタリゼーションを行っている。そして、大量合成法も検討し実用化の基盤を完成させている。

2章において金属系磁性微粒子の安定性の確保、微粒子形態および分布の制御、さらに大量合成法に至る基本技術とさらに高密度記録を達成するための金属系磁性微粒子の開発指針が完成した。この思想をもとに、第3章では、さらに金属系磁性微粒子としての特性を向上するため、鉄-コバルト合金メタル粉の開発を行った。鉄微粒子にコバルトを含有させるためには、鉄微粒子が体心立方格子という結晶構造を持つものに対して、コバルトは面心立方格子の結晶構造をもつ、そのため、原子状で均質に両者を混合したナノ磁性粉の開発を行った。その結果、コバルト含有率30%の合金磁性粉の調製を可能にした。この開発により、磁性微粒子のサイズを小さくすることにより、高密度記録が可能になった。また、それに伴い、耐酸化性を向上させるために、様々な添加元素を検討し、結果的にイットリウムが効果的に酸化を防止することが判明した。本研究により、現在実用化されている様々な磁気記録に用いられている磁性微粒子の基礎となった。

3章までの金属系磁性微粒子は、磁気異方性を利用した記録である。そのため、高密度記録を達成するために、粒子のサイズを小さくすると微粒子の長軸と短軸の長さの差が小さくなり、磁気異方性を利用した記録が困難となってくる。特に、1テラビットを超える記録密度の達成には磁気異方性を利用した記録は困難であり、異なる方式の記録を検討しなければならない。第4章では、先の困難を克服するため、結晶異方性を有する白金鉄ナノ磁性微粒子の開発を行った。その調製には、ポリオール法という独自に開発した方法により低温かつ飽和磁化5785eという fct 構造を有する PtFe ナノ粒子の調製を世界で初めて可能にした。

第5章は、本研究から得られた結果を総括して、将来の研究動向について述べている。

以上、本論文は、少エネルギー、少資源と言う21世紀の環境科学の思想をもとに、次

世代が要求する高密度、高信頼性の高い記録素材の開発を行ったもので、環境科学のみならず素材工学の発展に寄与するところが少なくない。

よって、本論文は博士（学術）の学位論文として合格と認める。