Frontiers of Science and Technology for the 21st Century
21世纪科技前沿丛书

Handbook of Advanced Magnetic Materials

Volume III Advanced Magnetic Materials: Fabrication and Processing

先进磁性材料手册

第3卷：先进磁性材料的制作和加工

Editors: David J. Sellmyer
Yi Liu
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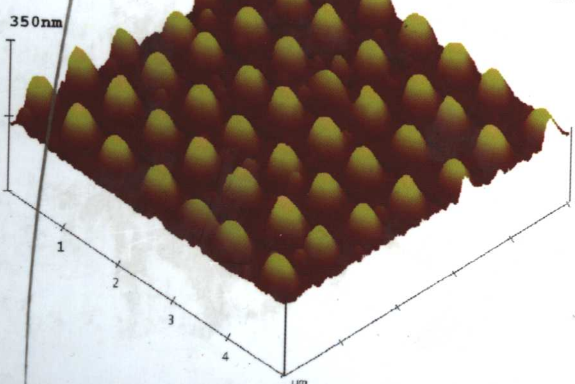

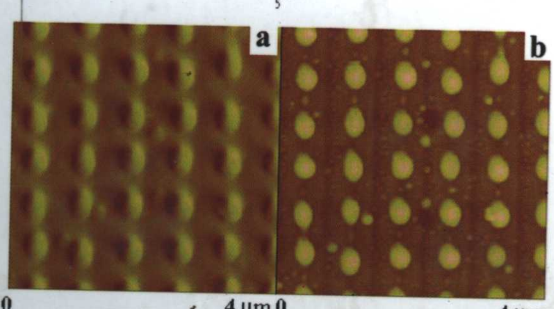

Tsinghua University Press
Springer

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内容简介

本书的目的是对磁性材料研究的新近进展提供一种全面的理解。本书共分四卷，每一卷集中论述一个具体的研究领域。每一章首先对该章的基本概念和重要观念进行阐述，然后从实验和理论方面进行详细地说明，最后介绍该领域的发展前景以及新的思想。书中提供了详尽的参考文献，可供研究人员参考。

每种新磁性材料的开发成功都取决于它的性能与成本。在正确的磁理论建立后，如何使用最合适的制作加工工艺是开发制造新磁性材料的关键。本卷对近年来各种磁性材料的制作加工原理和性能的相关性进行分析总结并瞻望未来。

本书的读者对象为相关专业的研究生和研究人员。

图书在版编目(CIP)数据

先进磁性材料手册 第3卷：先进磁性材料的制作和加工 = Handbook of Advanced Magnetic Materials Volume III Advanced Magnetic Materials: Fabrication and Processing/(美)塞尔米厄(Sellmyer, D. J.)，刘义(Liu, Yi)，(美)沙因多(Shindo, D.)主编. —北京：清华大学出版社，2005.7

ISBN 7-302-08606-0

Ⅰ. 现… Ⅱ. ①塞… ②刘… ③沙… Ⅲ. 磁性材料—英文 Ⅳ. TM271

中国版本图书馆 CIP 数据核字(2004)第 041659 号

出 版 者：清华大学出版社　　**地　址**：北京清华大学学研大厦

http://www.tup.com.cn　　**邮　编**：100084

社 总 机：010-62770175　　**客户服务**：010-62776969

组稿编辑：张兆琪

文稿编辑：韩燕丽

印 装 者：三河市春园印刷有限公司

发 行 者：新华书店总店北京发行所

开　本：153×235　**印张**：23.5　**字数**：575 千字

版　次：2005 年 7 月第 1 版　2005 年 7 月第1 次印刷

书　号：ISBN 7-302-08606-0/TB・73

印　数：1～1000

定　价：98.00 元

《Frontiers of Science and Technology for the 21st Century》

FOREWORD

Over the next several years, Tsinghua University Press will publish a series of books addressing progress in basic sciences and innovations in technology. We have made no attempt to pursue a comprehensive coverage of all disciplines of science and technology. Rather, topics for this series were selected with an emphasis on the currently active forefront of science and technology that will be contemporary in the next century. Most books in this series will deal with subjects of cross disciplines and newly emerging fields. Each book will be completed by individual authors or in a collaborative effort managed by an editor (s), and will be self-consistent, with contents systematically focused on review of the most recent advances and description of current progresses in the field. Sufficient introduction and references will be provided for readers with varying backgrounds. We have realize clearly the challenge of encompassing the diverse subjects of science and technology in one series. However, we hope that, through intensive collaboration between the authors and editors, high standards in editorial quality and scientific merit will be maintained for the entire series.

The international collaboration on this series has been coordinated by the Association of Chinese Scientists and Engineers-USA(ACSE). In the science community, authors voluntarily publish their results and discoveries in the full conviction that science should serve human society. The editors and authors of this series share this academic tradition, and many of them are fulfilling a spiritual commitment as well. For our editors and authors who were graduated from universities in China and further educated abroad in science and engineering, this is an opportunity to dedicate their work to the international education community and to commemorate the historical open-door movement that began in China two decades ago. When the human society enters the information age, there is no geographic boundary for science. The Editorial committee hopes that this series will promote further international collaboration in scientific research and education at the dawn of the new century.

The Editorial Committee
1999.6

《21世纪科技前沿》

丛书序言

由清华大学出版社出版的这套丛书是基础科学和应用科学领域内的专门著作。除了可作为研究生教材外，也可作为科研和工程技术人员的参考书。在丛书的题材选择中，着重考虑目前比较活跃而且具有发展前景的新兴学科。因此，这套丛书大都涉及交叉和新兴学科的内容。编写的方式大多由主编策划并组织本学科有影响的专家共同执笔完成，从而使每一本书的系统性和各章节内容的连贯性得到了充分的兼顾。丛书涵盖学科的最新学术进展，兼顾到基本理论和新技术、新方法的介绍，并引入必要的导论和充分的参考文献以适应具有不同学术背景的读者。编撰一套容纳多学科的科技丛书是一项浩繁的工作，我们希望通过主编和作者的集体努力和精诚协作，使整套丛书的学术水准能够保持在较高的水平上。

编辑《21世纪科技前沿》丛书是由“旅美中国科学家工程师协会”发起的一项国际科技界的合作。传递信息，加强交流，促进新世纪的科技繁荣是编著者们参与此项工作的共同信念。此外，这套丛书还具有特别的纪念意义。20年前，历史的进程使成千上万的中国学生、学者有机会走出国门，到世界各地学习和从事科学研究。今天，活跃在世界科技前沿领域的中华学子们没有忘记振兴祖国科技教育事业的责任和推动国际学术交流与合作的义务。正是基于这一共同的心愿，大家积极参与这套系列丛书的撰写、组稿和编辑工作。为此，我们愿以这套丛书来纪念中国改革开放20周年。

编委会

1999.6

Handbook of Advanced Magnetic Materials
Preface

In December 2002, the world's first commercial magnetic levitation supertrain went into operation in Shanghai. The train is held just above the rails by magnetic levitation (maglev) and can travel at a speed of 400 km/hr completing the 30km journey from the city to the airport in minutes. Now consumers are enjoying 50 GB hard drives compared to 0.5 GB hard drives ten years ago. Achievements in magnetic materials research have made dreams of a few decades ago reality. The objective of this book is to provide a comprehensive review of recent progress in magnetic materials research. The whole book consists of four volumes, each volume focusing on a specific field. Graduate students and professional researchers are targeted as the readers. Each chapter will have an introduction to give a clear definition of basic and important concepts of the topic. The details of the topic are then elucidated theoretically and experimentally. New ideas for further advancement are then discussed. Sufficient references are also included for those who wish to read the original work. Many of the authors are well known senior scientists. We have also chosen some accomplished young scientists to provide reviews on new and active topics.

In the last decade, one of the most significant thrust areas of materials research has been nanostructured magnetic materials. There are several critical sizes that control the behavior of a magnetic material. For example, the coercivity of a magnetic material made of particles increases with decreasing particle size, reaching a maximum where coherent rotation of a single-domain particle is realized, and then decreases with further decrease of the particle size. For a composite made of a magnetically hard phase and soft phase, when the grain size of the soft phase is sufficiently large, the soft and hard phases reverse independently. However, when the grain size of the soft phase is reduced to a size of about twice the domain wall thickness of the hard phase, the soft and hard phases will be exchange-coupled and behave as if a single magnetic phase is present. Such behavior can be used to increase the energy product of high-performance permanent magnets. Size effects become critical when dimensions approach a few nanometers, where quantum phenomena appear. The first volume of the book has therefore been devoted to the recent development of nanostructured magnetic materials, emphasizing size effects.

Our understanding of magnetism has advanced with the establishment of the theory of atomic magnetic moments and itinerant magnetism. In general, the magnetism of a bulk material can be considered as the superposition of atomic magnetic moments plus itinerant magnetism due to conduction electrons. In practical applications the situation becomes much more complicated. The boundary conditions have to be taken into account. This includes the size of the crystals, second-phase effects and intrinsic properties of each phase. The effects of magnetic relaxation over long periods of time can be critical to understanding. Simulation is a powerful tool for exploration and explanation of properties of various magnetic materials. Simulation also provides insight for further development of new materials. Naturally, before any simulation can be started, a model must be constructed. This requires that the material be well characterized. Therefore the second volume of the book provides a comprehensive review of both experimental methods and simulation techniques for the characterization of magnetic materials. After an introduction, each section gives a detailed description of the method and the following sections provide examples and results of the method. Finally further development of the method will be discussed.

The success of each type of magnetic material depends on its properties and cost which are directly related to its fabrication process. Processing of a material can be critical for development of artificial materials such as multilayer films, clusters, etc. Moreover, cost-effective processing usually determines whether a material can be commercialized. In recent years processing of materials has continuously evolved from improvement of traditional methods to more sophisticated and novel methods. The objective of the third volume of the book is to provide a comprehensive review of recent developments in processing of advanced magnetic materials. Each chapter will have an introduction and a section to provide a detailed description of the processing method. The following sections give detailed descriptions of the processing, properties and applications of the relevant materials. Finally the potential and limitation of the processing method will be discussed.

The properties of a magnetic material can be characterized by intrinsic properties such as anisotropy, saturation magnetization and extrinsic properties such as coercivity. The properties of a magnetic material can be affected by its chemical composition and processing route. With the continuous search for new materials and invention of new processing routes, magnetic properties of materials cover a wide spectrum of soft magnetic materials, hard magnetic materials, recording materials, sensor materials and others. The objective of the fourth volume of this book is to provide a comprehensive review of recent development of various magnetic materials and their applications. Each chapter will have an introduction of the materials and the principals of their applications. The following sections give a detailed description of the processing, properties and applications. Finally the potential and limitation of the materials will be discussed.

NASA is considering the launching of spacecraft by maglev. The first stage rocket, which accounts for two-thirds of the cost and is lost every launch, would be replaced by a maglev track. Using a 50 ft track NASA scientists have accelerated a model spacecraft to 96kph in less than half a second. In the last few decades the knowledge of mankind has been expanding rapidly into deep space measured by light years and the nano world where building blocks of atoms are being engineered. Magnetism and magnetic materials are among the most intriguing and fascinating science and engineering fields. Undoubtedly advances in magnetic materials research will continue to fuel our understanding of the universe in the new century. We hope this book will provide a useful reference for researchers working at the frontier of magnetic materials research.

We would like to express our sincere thanks to all our devoted authors, technical editors, and publishers for making this book possible.

The editors

Contents

1 HDDR Process for the Production of High Performance Rare-Earth Magnets

Satoshi Sugimoto and David Book

In this chapter the term "magnetic polarization" J is used, which is related to "magnetization" M and "magnetic flux density" B, by $J = \mu_0 M = B - \mu_0 H$, where magnetic constant (permeability of a vacuum) $\mu_0 = 4\pi \times 10^{-7}$ (H/m). In general, SI units were used instead of cgs units. However, the symbols and units in the figures were not changed from those used in the original papers, and so cgs units sometimes remain. In addition, for the units of magnetic field, both amperes/metre [A/m] (related to H) and Tesla [T] (related to $\mu_0 H$) were used.

1.1 Introduction

Permanent magnets are now essential components in many fields of technology, because of their ability to provide a magnetic flux, and they have applications in a wide range of devices (Fastenau and van Loenen, 1996). In the last few decades, the development of hard magnetic materials has been very rapid, with the advent of rare-earth (R) permanent magnets.

In the 1960s, a hexagonal $SmCo_5$ compound with the $CaCu_5$-type structure appeared as the first rare-earth high performance magnet (Strnat et al., 1967; Strnat, 1988). The compound has magnetic properties that are suitable for a permanent magnet, such as a large uniaxial magnetocrystalline anisotropy $\mu_0 H_A \sim 28$ T (H_A is anisotropy field [A/m]), a relatively high saturation magnetization ($J_s \sim 1.14$ T), and a high Curie temperature (T_C = 720 ℃). The energy product, $(BH)_{max}$, of this type of magnet reached 160 kJ/m^3 (20 MGOe). In an attempt to produce compounds with even higher magnetizations, the Co content was increased to give R_2Co_{17}. The Sm_2Co_{17} compound has a higher saturation magnetization ($J_s \sim 1.25$ T) and a higher Curie temperature than the $SmCo_5$ compound, however the anisotropy field is smaller. In 1968, Nesbit et al. (1968) reported that Cu-added $SmCo_5$ ingots (i.e., not processed by powder metallurgy) exhibited high coercivities (over 320 kA/m) after heat treatment, and Tawara and Senno (1968) reported a similar effect for Cu in $CeCo_5$ ingot alloys. These are the first reports of the development of a two-phase decomposed R-Co magnets. A compositional compromise was then developed, between the high magnetization of Sm_2Co_{17}

and the high magnetic hardness of $SmCo_5$, by a precipitation hardening process, which forms Sm_2Co_{17} phase surrounded by a $SmCo_5$-type boundary phase. This Sm_2Co_{17}-type alloy, with additions of Fe, Cu, and Zr, increased the maximum energy product to 264 kJ/m^3 (33 MGOe) (Mishra et al., 1981). The development of RCo-based permanent magnets has been reviewed in detail by Strnat and Strnat (1991).

The main disadvantage with these materials was the comparatively high cost of the Sm and Co, and so research began to focus on trying to find an Fe-based magnetic material, with similar properties. This eventually led to the joint announcement of the development of magnets based on the body centred tetragonal $Nd_2Fe_{14}B$ phase, by Croat et al. (1984a, b) using melt spinning, and Sagawa et al. (1984) using powder-metallurgy techniques which resulted in energy products greater than 288kJ/m^3 (36 MGOe). The magnetic characteristics of the new $Nd_2Fe_{14}B$ phase are $J_s = 1.61$ T, $\mu_0 H_A = 7.2$ T and $T_C = 312$ ℃. Due to their superior magnetic properties and low cost, the Nd-Fe-B magnets have rapidly replaced SmCo type magnets (with the exception of high temperature applications, due to the relatively low T_c of the $Nd_2Fe_{14}B$ phase). Since then, Nd-Fe-B magnets with a $(BH)_{max}$ over 400 kJ/m^3 have been produced commercially, by improving alloy and powder preparation, magnetic pressing, and surface coating (Herbst, 1991). Very recently, an energy product of 460 kJ/m^3 (57.6 MGOe) was reported by Kaneko (2000,2004).

The search for novel and improved hard magnets has continued, with the discovery of a number of promising magnetic materials such as the $ThMn_{12}$-type compounds (Ohashi et al., 1987; Mooij and Buschow, 1987), Sm_2Fe_{17} interstitially modified with nitrogen (Coey and Sun, 1990), $ThMn_{12}$-type (Yang, 1991) and $Nd_3(Fe,Ti)_{29}$-type (Collocott et al., 1992, Cadogan et al., 1994) compounds. The most notable of these compounds is $Sm_2Fe_{17}N_x$, which offers the prospect of magnets with even better magnetic properties and a high Curie temperature (476 ℃), compared to that of $Nd_2Fe_{14}B$ (Kobayashi, 1994; Fujii and Sun, 1995; Skomski, 1996).

There are two well-established techniques for the manufacture of rare earth permanent magnets: powder metallurgy is used to obtain high performance, anisotropic, fully dense magnet bodies; and melt-spinning is widely used to produce magnet powders for isotropic bonded magnets. Although the magnetic properties (i.e., the energy product) of near fully dense sintered magnets are superior, the ability to fabricate components to near net shape using coercive powder is often a more important factor (and which according to Fastenau (1996) and Luo (1999), has lead to bonded Nd-Fe-B magnets becoming the most rapidly growing sector of the permanent magnet market).

A more recent technique is the Hydrogenation, Disproportionation, Desorption, and Recombination (HDDR) process, which consists of a series of heat treatments in hydrogen and under vacuum. HDDR has proved to be an effective and economic way of obtaining powders for use in the production of high performance, anisotropic bonded magnets.

There have been a number of articles that have reviewed aspects of the HDDR process (Harris, 1996; Gutfleisch and Harris, 1996; Buschow, 1997; Gutfleisch and Harris, 1998). In this chapter, we review the history of the HDDR process, including recent improvements in the processing conditions used for the production of anisotropic Nd-Fe-B HDDR powders, and HDDR phenomena in other rare-earth iron (R-Fe) based compounds.

1.2 HDDR Phenomena in Nd-Fe-B

The HDDR process was first reported in Nd-Fe-B magnets by Takeshita and Nakayama (1989, 1990), and the reaction mechanisms involved were clarified by McGuiness et al. (1990a, b) and Harris and McGuiness (1990). A schematic illustrationof the conventional HDDR process is shown in Fig. 1.1. In this process, the Nd-Fe-B ingot is heated to ~700−900 ℃ (which is often accompanied by the decrepitation of the ingot into powder) and kept at this temperature under hydrogen, and then heat-treated under vacuum. After cooling under vacuum, a coercive powder is obtained which can be used to form bonded magnets. This process consists of four steps: hydrogenation of $Nd_2Fe_{14}B$; disproportionation of $Nd_2Fe_{14}B$ into $NdH_{2+\delta}$, α-Fe, and Fe_2B; desorption of hydrogen gas from $NdH_{2+\delta}$; and finally, recombination to the $Nd_2Fe_{14}B$ phase. During this process grain refinement occurs, resulting in a

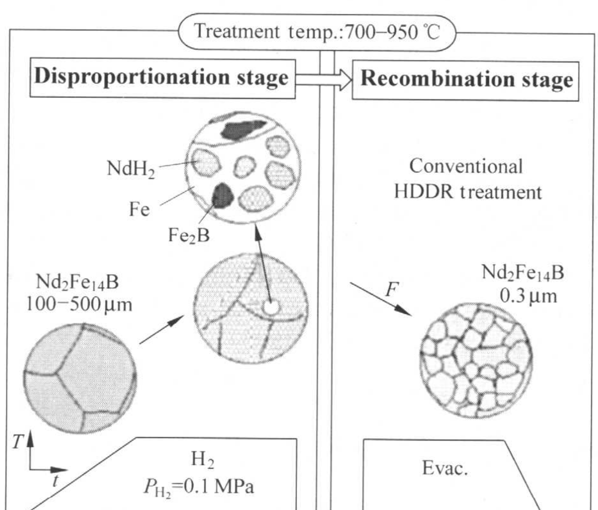

Figure 1.1 Schematic illustration of the HDDR process in Nd-Fe-B.