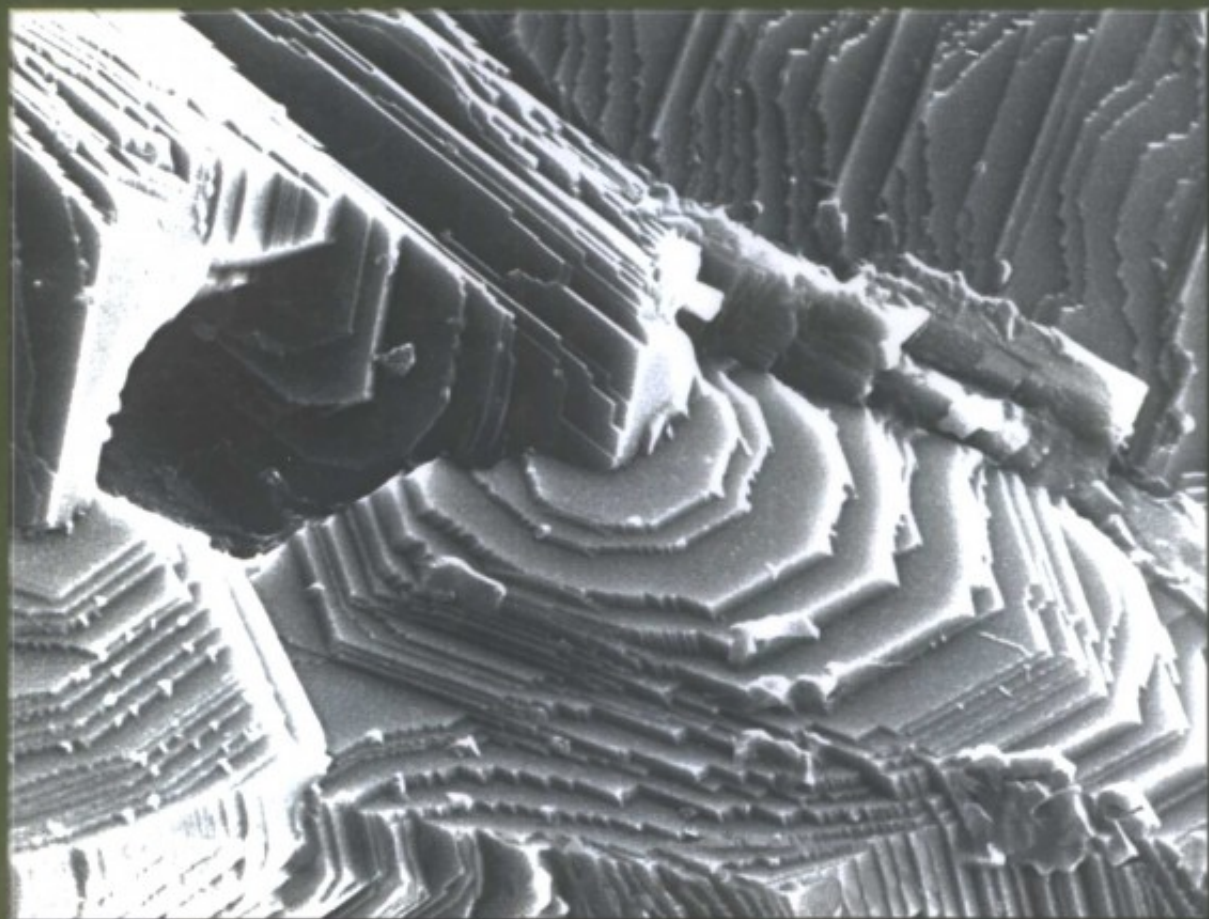




# 耐火材料显微结构

高振昕 平增福 张战营 编著  
黄振武 任刚伟 卫晓辉



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黄振武 任刚伟 卫晓辉 编著

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2002

# **Microstructur of Refractories**

Eds. by Gao Zhenxin, Ping Zengfu, Zhang Zhanying,  
Huang Zhenwu, Ren Gangwei, Wei Xiaohui

Beijing

Metallurgical Industry Press

2002

2002.5.10/10

## 内 容 提 要

本书是一部以相的形貌和共生组合的图像内容为基础素材,来论述耐火材料显微结构的形成与演变的理论专著。全书共9章,涉及硅砖、高铝砖、烧结和电熔莫来石、刚玉制品、烧结和熔铸 AZS 制品、镁铬系制品、方镁石-尖晶石系制品、镁-钙-铁系材料、含炭制品和 SiAlON 结合制品等诸多品种。

一定化学组成的制品具有其相应的显微结构内容。制品虽由同一化学组成,但以不同原料生产的制品可能呈现出各种各样的显微结构;而当某些工艺参数改变时,还会使显微结构细节变异。这也正是要求通过显微结构分析来确认和评价耐火材料生产工艺与性能之间相关性的重要原由。

耐火材料在高温与化学侵蚀作用下将发生具有段带特征的显微结构变化,通过分析这种变化的过程,可以掌握各种热工窑炉的损毁机制。例如,炼钢电炉所用的炉顶高铝砖、炉壁 MgO-C 砖和炉底 MgO-CaO-Fe<sub>2</sub>O<sub>3</sub> 系捣打料;炼钢转炉衬砖和溅渣补炉层,各种炉外精炼炉用碱性制品,高炉和热风炉衬砖,盛钢桶用各种内衬材料,玻璃熔窑所用顶砖、熔池熔铸和烧结 AZS、锡槽底砖和蓄热室碱性砖,水泥回转窑衬砖等各类耐火材料的蚀变现象各具特点,机制各异。

熔融-析晶、烧结-晶体长大、化合、分解、相变、蒸发、氧化-还原等反应过程造成的新生相组合形貌,新奇悦目,精美绝伦,足令欣赏者陶醉。本书中展示了许多这样的显微结构照片。

本书适用于从事耐火材料的科研工作者、工程技术人员阅读,亦可作为教材参考书。

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耐火材料是无机非金属材料(广义陶瓷材料)中的一个重要组成部分。与其他材料的主要区别在于:它要经受高温下热的、化学的和力学的作用而不破坏,以确保各类热工设备的正常作业和长寿。耐火材料的使用行为与其显微结构的形成和演变有着密切的联系。

显微结构分析是一门以结晶学、矿物学、岩石学、地质学和物理化学等为基础理论并且与工艺学相结合的实验科学,借以解释生产和使用中的各种现象和机理。从事此业者既有矿物-岩石学者,也有工艺学者。矿物-岩石学家掌握显微术,而剖析工业产品,就需要了解工艺学;工艺学者要研究产品显微结构与工艺-性能的关系,要掌握显微术,就需要学习相关的基础知识。总之,从事材料科学和工程的人们需具备两方面的知识,且以材料科学的观点来论证显微结构。所有的工程专家都知道显微结构研究是改进工艺和提高产品质量的重要基础,甚至被概括为:现代材料科学的核心问题是显微结构的研究。近 20 年来,国内、外耐火材料的工艺水平都得到了空前的提高,进入了一个新的科技时代,无以数计的高功能、高性能的新材料被开发出来,促进了冶金、建材、陶瓷、化工等行业的发展。一些新制品,正是在剖析了使用损毁机理并设计出合理的显微结构的基础上研制成功的。许多耐火材料生产者 and 使用者都深刻地领悟到显微结构研究在生产工艺-使用性能之间的核心和纽带作用,因而也使显微结构分析备受重视。

从 20 世纪 50 年代开始,许多高校的无机非金属材料专业就开设了显微学课程。但如上实验课时,却缺少足够的样品和文字资料供学生参考。一些外文版教材的实例内容也很简略。1972~1973 年,西安建筑科技大学杨兴华教授、鞍山科技大学沈端书教授和华南理工大学赵子衷教授来院做学术交流,为学校开设耐火材料显微结构分析课程搜集资料。当时,虽有各种原料和制品的薄片和光片供观察,却没有系统的文字材料。

1977 年,应一些单位的要求,我院举办了一个显微结构分析学习班。为给学员提供样品鉴定的辅导材料,笔者整理了过去 20 多年来分析过的各种耐火材料(包括从国外引进的)试样及其使用后的样品的显微结构分析报告,归纳成 9 个系列,草就《耐火材料显微结构讲义》(含百余帧显微照片)供大家参考,这便是本书的最初蓝本。

1986 年,根据国家重点图书出版计划,由诸培南、翁臻培、王天颐任主编,组织 30 多位作者成立编委会,着手编写《无机非金属材料显微结构图册》。这是一部以大量显微照片为基本素材的、阐述各种材料显微结构的形成和演变的专著,从内容到形式均颇新颖,在国内、外诸多专著中尚无相似者,尤以显微图片之多、之佳而堪称一最,而所有这些照片皆出自作者之手。笔者在该书中撰写了“耐火材料”一章。1994 年,历经 8 年时间,这部凝聚着众多显微学工作者心血的书终于出版了。该书被评为优秀获奖作品。

1993 年,浙江大学周志朝教授根据国家出版规划,编写《硅酸盐岩相学》教材,邀笔者撰写“耐火材料”一章并合写总论。笔者建议将书名改为《无机材料显微结构分析》,获上级批准。既考虑到教材的继承性,又联系到新仪器、新技术的应用,遂对基础部分的内容和格式也作了改写。该书 2000 年再版,被评为国家级优秀教材。

1999 年秋,西安建筑科技大学蒋明学教授邀笔者为材料系研究生班讲授耐火材料显微结构。正是以此为契机,会同几位同行编写了这部《耐火材料显微结构》。它承袭了《无机非金属材料显微结构图册》的编写原则,内容皆为作者的实践总结。不过,本书只保留了 1977 年《耐火材料显微结构讲义》中的有限内容,而以近年的资料为重点。

本书划分 9 章。总论一章概述了显微结构的定义和与其他学科的关系并从学术著作和仪器发展两方面介绍了无机非金属材料显微结构分析的百余年历史,追忆了各国学者的辛勤劳动和卓越贡献。其余 8 章以化学体系为类,分别论述了硅砖、高铝砖、烧结和电熔莫来石、刚玉制品、烧结和熔铸 AZS 制品、镁铬系制品、方镁石-尖晶石系制品、镁-钙-铁系材料、含碳制品和 SiAlON 结合制品等诸多品种。一定化学组成的制品具有其相应的显微结构内容;同一化学组成但以不同原料生产的制品可能呈现出各种各样的显微结构,而当某些工艺参数改变时,还会使显微结构细节变异。这也正是要求通过显微结构分析来确认和评价耐火材料生产工艺与性能之间相关性的重要原因。耐火材料在高温与化学侵蚀作用下将发生具有段带特征的显微结构变化,通过分析这种变化的过程,可以掌握各种热工窑炉的损毁机制。

学术研究倡导问题意识。随着时间的推移、知识的更新和仪器的发展,对某些被认为是熟知的、经典的理论、概念和结论,将会形成新的认识或疑问。国际间耐火材料显微结构研究的近百年历史中,20 世纪 60~70 年代以来进展迅速。从一批著名显微学家的工作中,我们吸取到了有益的经验,也掌握了衡量显微结构分析国际水平的尺度。借本书提供的、有限的参考文献可以概略地了解这一历程各国学者的成就和对一些问题的争论。作者不囿于一家之见,而是尽量展示不同的观点,读者可按图索骥,结合实践探求各自的理解。

就本书的内容看,它包括了作者 1956~2001 年间的研究工作。这期间亦包含了诸多同事在化学、XRD、电镜分析和制样等工作中或在其他方面给了笔者以极大的帮助和支持,他们或与笔者合作发表过论文或为作者提供了宝贵的样品,皆为本书做出了贡献。只缘有了这些基础素材,方能撰写此书,作者向他们谨致谢忱!

本书初稿经陈显求教授、翁臻培教授、李香庭教授和翁润生教授审阅,提出了许多宝贵意见,作者多次修改。苏良赫教授年事已高,然精神矍铄,也热情地审阅了书稿。《耐火材料显微结构》一书的出版也得到了洛阳耐火材料研究院同事们的大力支持,在此一并致以深谢!

由于作者学识水平所限,挂一漏万或谬误之处在所难免,敬请有识者批评、指正。

高振昕  
2001 年仲秋

## FOREWORD

Refractories are of an important part in inorganic nonmetallic materials, generally referred to as ceramic materials. The major difference with other materials is that they are subject to thermal, chemical and mechanical attacks at high temperatures. Purposely designed and known performances are needed to ensure the thermal devices lined with them to work safely and durably, to minimize heat and mass transfer losses. The performances of refractories have a close relationship with the formation and evolution of their microstructure.

Microstructure analysis is an experimental science based on crystallography, mineralogy, petrography, geology, physics, chemistry, etc. in cooperation with manufacture technologies. It helps interpret multifarious phenomena and reveal the related mechanisms in the manufacture and application of refractories. People engaged in this kind of occupation include not only petrographers and mineralogists, but also the manufacturing technologists. The petrography and mineralogy workers skilled in microscopy need to get acquainted with some knowledge of manufacture technology, when to analyze industrial products; while the technologists need also to learn and use microscopy to reveal and understand the relationship among microstructure, processing parameters and properties of industrial products. After all, materials scientists and engineers need a good command of the knowledge in both aspects mentioned above and should deal with microstructure from the point of view of material science. Most materials scientists and engineers may agree that the study on microstructure is an important basis for improving the production and quality of products. It has even come down to the well accepted point that the key issue in modern material science is the microstructure study. Since recent two decades, both at home and abroad, the manufacturing technology of refractories has got unparalleled advancement and the refractories industry has entered a new era full of science and technology, represented by that countless high performance and functional refractories have emerged in, which have greatly promoted the rapid development of the metallurgy, cement, glass, ceramics, chemical and other user industries. It is the study on wear mechanism, by means of microscopy in most cases, plus the optimization in microstructure that has resulted in many new advanced refractory products. Refractories workers, both from manufactures and from end users, have clearly seen

the linking role of microstructure study in the improvement and optimization of manufacturing technology and service performance of refractories. These have made the microstructure analysis be attached increasing importance.

Since the fifties of the 20th century, courses on microscopy have been offered in many colleges and universities with the specialities in inorganic materials. For experimental trainings, however, there was a certain lack of reference samples and reading materials for students. The cases in some foreign teaching materials appeared also too sketchy. In 1972~1973, Prof. Yang Xinghua at Xi'an Architecture Science and Technology University, Prof. Shen Duanshu at Anshan Science and Technology University and Prof. Zhao Zizhong at Hua'nan Science and Technology University came to Luoyang Institute of Refractories Research (LIRR) for academic exchanges and collecting data for the course of microstructure analysis on refractories. At that time there were although various sections and polished sections of refractory raw materials and products for observing by optical microscopy, there were few systematic text materials available from LIRR.

In 1977, upon the requests of some institutions and companies, a training course of microstructure analysis was offered by LIRR. To provide the attendants some guidance materials, the author sorted out the written reports of microstructure analysis on all the analyzed samples of refractories before or after use, since 20 years, including those imported from abroad, divided them into 9 series and wrote a book named "Teaching Materials on the Microstructure of Refractories", in which more than 100 micrographs were inserted. That can be taken as the very original version of the present book.

In 1986, according to the national publishing plan of key books, an editorial board was set up, consisting of more than 30 experts with Zhu Peinan, Weng Zhenpei and Wang Tiandi as the editor-in-chief, to compile the book named "Microstructure of Ceramics". This is a monograph, with a lot of micrographs, on the formation and evolution of microstructure of various materials, distinguished from others both in its form and its content, in particular the quantity and quality of the micrographs all taken by the authors themselves. I contributed the chapter 2 "Refractories" for that book. Eight years after in 1994, the book, as an embodiment of many microscopy workers' painstaking efforts, was at last published and was nominated as one of the national outstanding publication works.

In 1993, in response to the national publishing plan, Prof. Zhou Zhichao at Zhejiang University began to devote himself to the textbook "Petrography of Silicate". He invited me to write a chapter on refractories and to co-write the General

Introduction. With adopting my suggestion, the name of the book was changed to "Microstructure Analysis of Inorganic Nonmetallic Materials". To take into account of the succession to the existed such books and the applications of new instruments and new techniques, the content and the pattern of the basic part in the book was renewed. This book was reprinted in 2000 and was chosen as among the national outstanding textbooks.

In the autumn 1999, Prof. Jiang Mingxue at Xi'an Architecture Science and Technology University invited me to lecture the microstructure of refractories for the postgraduate class. Taking this opportunity, the author, in cooperation with a few colleagues, worked out this book named "Microstructure of Refractories". It followed the writing principle of the *Microstructure of Ceramics* and the content was based on the author's practical work over the years. It preserved limited part of the *Teaching Materials on the Microstructure of Refractories* finished in 1977, but was added and given prominence to the data obtained in more recent years.

The present book consists of 9 chapters. A general introduction makes Chapter 0, covering the definition of microstructure, the connection of microstructural analysis with other subjects and a review, from the published works and the progress in measuring techniques, on the development of microstructure analysis of inorganic nonmetallic materials in a history of 100 years or so, in retrospect of the arduous efforts and prominent contributions made by researchers worldwide. The rest 8 chapters, cataloged according to chemical system, are on silica bricks, high alumina bricks, sintered or fused mullite and corundum products, sintered or fused  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-SiO}_2$  products,  $\text{MgO - Cr}_2\text{O}_3$  products, periclase - spinel products,  $\text{MgO-CaO-Fe}_2\text{O}_3$  refractories, carbon containing and Sialon bonded refractories, respectively. Chemical composition has of course an effect, but not the one and only, on microstructure of a product, it depends also on the sort of raw materials, which may give the same chemical composition of the product but different microstructure; the processing parameter is another key factor influencing microstructure details of a product. That is why to use microstructure analysis as the right way to confirm and evaluate the correlation between production and property of refractories. On the other hand, a refractory after high temperature and/or chemical attack in use will change to form different zones with characterized microstructure, by analyzing which via microscopy, it will help reveal and understand the deterioration mechanisms of the linings of various thermal equipment. Through the text and the cases in these chapters, readers may have a good comprehension of the points.

Scientific research calls for the sense of questioning. With the elapse of time,

updated knowledge and the advance in measuring technique, many well known, well accepted and classical theories and concepts are facing challenges. In the past 100 years or so of the history in microstructure study of refractories, the time since 1960~1970s of the 20th century has witnessed a rapid development. From the published work by many famous microscopy researchers, we have learnt their useful experience and held the yardstick for the international level of microstructure analysis. From the references that this book has offered, though limited, readers can access briefly the accomplishments worldwide and the arguments on some issues. To avoid being constrained in one-sided viewpoint, the author has as much as possible introduced different standpoints. Such a clue may help lead readers to further particular comprehension, combining with their own practice.

From the content of the present book, it has embodied the author's research work from 1956 to 2001. In this long period many colleagues have offered a lot of helps and supports in chemical analysis, XRD analysis, SEM analysis, samples preparation, etc. or in whatsoever the other ways. They have either co-authored papers with the author or offered appreciable samples. All these are of invaluable contributions to this book. Without them, it would be impossible for this book to come out. Many heartfelt thanks are owed to them!

I, also on behalf of the co-authors, would like to thank Prof. Chen Xianqiu, Prof. Weng Zhenpei, Prof. Li Xiangting and Prof. Weng Runsheng for their valuable suggestions in going over the book, many of which have been adopted. Special thanks are due to respectful Prof. Su Lianghe who is at his advanced age but still in high spirits in going over this book. We acknowledge also our sincere gratitude to the investigators of LIRR for their constant support and encouragement.

We sincerely welcome any comments or criticisms on whatever the readers will find. From the imperfections or mistakes that may have hidden in the book due to the limitation in our personal knowledge, we can learn more and make improvements. So please do communicate with us. Thank you in advance.

Gao Zhenxin

In the mid autumn of 2001

## 图例说明

1. 显微照片以章为序,如 1-1 表示第 1 章显微照片之 1;2-1 表示第 2 章显微照片之 1;3-30 表示第 3 章显微照片之 30……依此类推。其他附图,如相图、衍射图谱、曲线图和方框图等亦以章为序,但不与显微照片一起编序;另以 *a. b. c. d. ……*,表示之,如图 1-*a*;2-*b*;3-*e*……等。

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