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The treatment of sintered stainless steels in this book addresses the need to more clearly understand the many factors that affect the corrosion resistance of powder metallurgy (PM) stainless steels. For over a half-century, PM technology has been an effective method of net shape processing to produce structural parts for the automotive and other industries. Conflicting literature on the factors that influence the corrosion resistance of PM stainless steels has led to some widespread misconceptions, which generally attribute poor corrosion resistance to just the presence of pores (whereby the presence of pores increases the effective surface area of a sintered part and thereby increases the corrosion rate in the passive region). A crevice-sensitive density region does exist in which a neutral chloride environment can give rise to crevice corrosion. Nonetheless, many or most cases of underperformance cited can be traced to inappropriate sintering practices that result in poor metallurgical soundness.

Recent progress in the understanding of corrosion and corrosion-resistance properties of sintered stainless steels has led to renewed interest in their application in the automotive sector for the benefit of net-shape processing and more efficient materials utilization. To obtain good corrosion-resistance properties, sintered stainless steels require careful processing, starting with powder selection, avoidance of contamination, efficient delubrication, and through to controlled sintering and cooling. There are several distinct, process-related corrosion issues with sintered stainless steels that the PM industry had to cope with over the years:

- Contamination with less noble constituents, causing galvanic corrosion
- Crevice-corrosion-prone density range in neutral saline environments
- Excessive carbon content (from various sources), causing sensitization and intergranular corrosion
- Excessive nitrogen content, due to sintering in H₂–N₂ mixtures containing large amounts of nitrogen (i.e., dissociated ammonia), in combination with slow cooling rates produces sensitization and intergranular corrosion
- Inadequate cooling after sintering, which, in the presence of excessive carbon, can cause sensitization and intergranular corrosion
- Excessive dewpoints and/or inadequate cooling causes reoxidation during cooling and susceptibility to pitting
- Surface chromium losses due to sintering in a vacuum furnace can impair the corrosion resistance of sintered stainless steels
- Pitting corrosion due to incomplete reduction of original residual oxides.

Solutions to all of these problems are at various stages of implementation in the industry. Because of this, and the fact that corrosion resistance is usually the prime property when stainless steel is selected as a material, the subject of PM stainless steel processing, and, more specifically, of optimal processing, from powder to final part pervades the entire book.

For stainless steel parts manufacturers, this book serves as a guide to making parts that possess improved corrosion-resistance properties, thereby opening new market opportunities. Although
some of the aforementioned problems can also be present in wrought and cast stainless steels, some are specific to PM, and all have special PM processing-related characteristics. The general approach is first to present the phenomenological aspects of a subject, including problem areas. This is followed by a description of its underlying principles and then a discussion and illustration of available solutions. The perspectives taken are often those of a powder producer, reflecting the authors’ affiliation. Significant portions of the data are from Professor Maahn and coworkers of the Technical University of Denmark, who, in a three-year effort (1990 to 1993) in cooperation with industry, made important contributions to this subject.

The structure of the book more or less follows the sequence of the production process. After a brief historical background, the chapters include metallurgical background and alloy compositions, powder manufacture and properties of powders, compaction and shaping, sintering and corrosion, optimal sintering and surface modification, with concluding chapters on mechanical and magnetic properties, corrosion-resistance testing and properties, secondary operations, and applications. Emphasis is concentrated on the press-and-sinter technology of PM, although some consideration is given to metal injection molding, powder extrusion, and hot isostatic pressing. The discussion of optimal sintering in Chapter 6, “Alloying Elements, Optimal Sintering, and Surface Modification in PM Stainless Steels,” although based largely on press-and-sinter technology, is relevant, with appropriate restrictions, to other modes of PM shaping and consolidating.

Introductory books on PM and corrosion science provide a useful basis for this text, because the reader is assumed to possess a basic knowledge of metallurgy, powder metallurgy, and corrosion science. Suggested references are Powder Metallurgy Science by R.M. German (Ref 1); Powder Metal Technologies and Applications, Volume 7, ASM Handbook, 1998 (Ref 2); Corrosion Engineering by M.G. Fontana (Ref 3); Corrosion and Corrosion Control by H.H. Uhlig and R.W. Revie (Ref 4); and Corrosion: Fundamentals, Testing, and Protection, Volume 13A, ASM Handbook, 2003 (Ref 5). Standards on metal corrosion are found in Volume 3.02 of the Annual Book of ASTM Standards. Nevertheless, the authors have attempted to keep the text simple and to facilitate understanding through the use of numerous pictures, illustrations, and references. A brief glossary of definitions of powder metallurgy and corrosion terms is shown in an Appendix, with more complete versions available in ASTM standard B-243 (Ref 6) and in the aforementioned ASM Handbook on corrosion.

In this context, it is hoped that this work provides a contribution to the more effective processing of sintered stainless steels to achieve improved corrosion resistance and successful applications in more demanding environments. Evidence for this is presented, and the authors believe that it will be only a matter of time until the versatility of the PM process closes any gaps that still exist with wrought or cast forms. As the industry implements the solutions to the previously mentioned problems, knowledge from wrought and cast stainless steel technology can be used and applied more effectively to PM stainless steels. This then should develop into a more comprehensive use and representation of PM stainless steels within the overall field of metals technology.

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References
1. R.M. German, Powder Metallurgy Science, Metal Powder Industries Federation, 1994
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