

S E C O N D E D I T I O N

EXTRACTIVE METALLURGY OF RARE EARTHS



Nagaiyar Krishnamurthy
Chiranjib Kumar Gupta



CRC Press
Taylor & Francis Group

EXTRACTIVE METALLURGY OF RARE EARTHS

S E C O N D E D I T I O N

EXTRACTIVE METALLURGY OF RARE EARTHS

S E C O N D E D I T I O N

Nagaiyar Krishnamurthy
Chiranjib Kumar Gupta



CRC Press

Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2016 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works
Version Date: 20151008

International Standard Book Number-13: 978-1-4665-7638-4 (eBook - PDF)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

Sri Krishnarpanam

Contents

Preface to the Second Edition	xxi
Preface to the First Edition	xxv
Authors	xxix

Chapter 1	The Rare Earths	1
1.1	Introduction	1
1.2	Discovery	1
1.3	Special Characteristics	8
1.3.1	Electronic Configuration	8
1.3.2	Lanthanide Contraction	19
1.3.3	Basicity	20
1.4	Properties	21
1.4.1	Melting Point	21
1.4.2	Boiling Point	22
1.4.3	Allotropes	23
1.4.4	Resistivity	23
1.4.5	Magnetic Properties	24
1.4.6	Spectral Properties	24
1.4.7	Mechanical Properties	25
1.5	Reactivity	25
1.5.1	Air/Oxygen	25
1.5.2	Refractories	26
1.5.3	Nitrogen	26
1.5.4	Hydrogen	28
1.5.5	Carbon	28
1.5.6	Silicon	28
1.5.7	Sulfur, Selenium, Phosphorus	28
1.5.8	Refractory Metals	29
1.5.9	Acids and Bases	29
1.5.10	Water	30
1.6	Aqueous Systems	30
1.6.1	Trivalent State	30
1.6.2	Complexes	31
1.6.3	Tetravalent State	31
1.6.4	Divalent State	32
1.7	Applications	33
1.7.1	Metallurgy	34
1.7.1.1	Ductile Iron	34
1.7.1.2	Steels	36
1.7.1.3	Superalloys	40
1.7.1.4	Magnesium Alloys	41

1.7.1.5	Aluminum Alloys	41
1.7.1.6	Titanium Alloys	42
1.7.1.7	Copper Alloys	42
1.7.1.8	Zinc Alloys	42
1.7.1.9	Oxide Dispersion–Strengthened Alloys	43
1.7.1.10	Long-Range-Ordered Alloys	43
1.7.2	Magnets	43
1.7.3	Terfenol.....	51
1.7.4	Magnetic Refrigeration	53
1.7.5	Ceramics.....	53
1.7.6	Electronics.....	56
1.7.7	Chemical	57
1.7.8	Optical	59
1.7.9	Phosphors	61
1.7.9.1	Technology Transition in High-Efficiency Lighting	64
1.7.10	Nuclear	66
1.7.11	Hydrogen Storage	67
1.7.12	Superconductor.....	70
1.7.13	Miscellaneous.....	70
1.8	Global Rare-Earth Demand.....	73
1.9	Summary	81
Chapter 2	Resources	85
2.1	Introduction	85
2.2	Crustal Abundance	86
2.3	Minerals.....	87
2.3.1	Bastnasite.....	88
2.3.2	Monazite.....	93
2.3.3	Xenotime	94
2.3.4	Allanite.....	94
2.3.5	Apatite	97
2.3.6	Brannerite	99
2.3.7	Eudialyte	99
2.3.8	Euxenite, Fergusonite, Florencite, Gadolinite, and Loparite	99
2.3.9	Perovskite	100
2.3.10	Pyrochlore	100
2.3.11	Zircon	100
2.3.12	Others	101
2.3.13	Scandium Minerals	102
2.3.14	Promethium	102
2.4	Rare-Earth Deposits	102
2.4.1	Basic Geology of REEs	102
2.4.2	Distribution.....	105

2.5	Resources and Reserves	107
2.6	Occurrence	163
2.6.1	Argentina.....	163
2.6.2	Australia	163
2.6.2.1	Brown's Range	163
2.6.2.2	Dubbo Zirconia Project (DZP), Toongi	164
2.6.2.3	Eneabba.....	164
2.6.2.4	Cooljarloo/Jurien Bay	164
2.6.2.5	Cummins Range	165
2.6.2.6	Gilgai Intrusion.....	165
2.6.2.7	Jangardup.....	165
2.6.2.8	WIM-150.....	165
2.6.2.9	Murray Basin	165
2.6.2.10	Nolans Bore	165
2.6.2.11	Norraburra RE Deposit.....	166
2.6.2.12	Olympic Dam.....	166
2.6.2.13	Brockman (Hastings) Deposit.....	166
2.6.2.14	Mary Kathleen.....	166
2.6.2.15	Mount Weld	167
2.6.2.16	John Galt.....	168
2.6.2.17	Radium Hill	168
2.6.2.18	Syerston.....	168
2.6.2.19	Thuddungra.....	168
2.6.2.20	Yangibana	168
2.6.3	Bangladesh	168
2.6.4	Brazil	169
2.6.5	Canada.....	170
2.6.5.1	Denison Mine	170
2.6.5.2	Nechalacho/Thor Lake Mine Site, Northwest Territories	170
2.6.5.3	Yukon.....	171
2.6.5.4	Hoidas Lake.....	171
2.6.5.5	Kipawa	171
2.6.6	China	172
2.6.6.1	Bayan Obo	172
2.6.6.2	Ion-Adsorption Ore.....	175
2.6.6.3	Placers.....	176
2.6.6.4	Other Deposits	176
2.6.7	Egypt	177
2.6.8	Germany	177
2.6.9	Greenland	177
2.6.9.1	Kvanefjeld.....	177
2.6.10	India.....	178
2.6.10.1	Hard Rock Deposits	178
2.6.10.2	Placers.....	179
2.6.11	Indonesia	179

2.6.12	Japan.....	180
2.6.13	Kenya.....	180
2.6.14	Madagascar	180
2.6.15	Malaysia	180
2.6.16	Malawi.....	181
	2.6.16.1 Kangankunde.....	181
	2.6.16.2 Nanthace Hill.....	181
	2.6.16.3 Songwe.....	182
	2.6.16.4 Chilwa Island	182
2.6.17	Mozambique	182
2.6.18	Myanmar	182
2.6.19	New Zealand	182
2.6.20	Peru.....	182
2.6.21	South Africa	182
	2.6.21.1 Buffalo Fluorspar.....	183
	2.6.21.2 Phalaborwa Complex	183
	2.6.21.3 Steenkampskrall	183
	2.6.21.4 Zandkopsdrift	183
2.6.22	Sri Lanka	184
2.6.23	Sweden	184
2.6.24	Taiwan	184
2.6.25	Thailand	185
2.6.26	Turkey.....	185
2.6.27	United States	185
	2.6.27.1 Elk Creek Carbonatite, Nebraska	186
	2.6.27.2 Music Valley, California.....	186
	2.6.27.3 Wet Mountains Area, Colorado.....	186
	2.6.27.4 Diamond Creek Area, Idaho.....	187
	2.6.27.5 Hall Mountain, Idaho	187
	2.6.27.6 Lemhi Pass District, Idaho	187
	2.6.27.7 Pea Ridge Iron Deposit and Mine, Missouri.....	188
	2.6.27.8 Hicks Dome, Illinois.....	188
	2.6.27.9 Mineville Iron District, New York	188
	2.6.27.10 Bear Lodge Mountains, Wyoming	189
	2.6.27.11 Mountain Pass, California	189
	2.6.27.12 Bokan Mountain, Alaska.....	190
	2.6.27.13 Iron Hill, Colorado	190
	2.6.27.14 Gallinas Mountains, New Mexico.....	190
	2.6.27.15 Pajarito, New Mexico	190
	2.6.27.16 Placers.....	190
2.6.28	Former Soviet Union	192
	2.6.28.1 Tomtor.....	193
	2.6.28.2 Chuktukon	193
	2.6.28.3 Kyrgyzstan	194

2.6.29	Venezuela	194
2.6.30	Vietnam	194
2.6.30.1	Nam Xe	194
2.6.30.2	Dong Pao.....	195
2.6.31	Zaire	195
2.7	By-Products and Coproducts	195
2.8	World Rare-Earth Production.....	197
2.8.1	Brazil	202
2.8.2	India.....	203
2.8.3	United States	203
2.8.4	Australia	205
2.8.5	China	207
2.8.6	Former Soviet Union	210
2.8.7	South Africa	211
2.8.8	Canada.....	211
2.8.9	Malaysia	212
2.8.10	Thailand	212
2.8.11	Sri Lanka.....	212
2.8.12	Zaire and Madagascar	213
2.9	Scenario for the Immediate Future	213
2.10	Summary	229
Chapter 3	Resource Processing.....	235
3.1	Introduction	235
3.2	Mining	236
3.2.1	Hard-Rock Deposits	236
3.2.2	Placer Deposits	236
3.3	Physical Beneficiation.....	236
3.3.1	Monazite.....	239
3.3.1.1	Froth Flotation	244
3.3.1.2	Bastnasite Flotation	244
3.3.1.3	Monazite Flotation.....	246
3.3.2	Bastnasite.....	247
3.3.3	Bayan Obo Ore.....	249
3.4	Beneficiation of Other Rare-Earth Minerals	251
3.5	Chemical Treatment	254
3.5.1	Monazite.....	254
3.5.1.1	Acid Treatment	254
3.5.1.2	Alkali Treatment.....	255
3.5.1.3	Indian Rare Earths Ltd. Practice	255
3.5.1.4	Monazite Breakdown Practices	258
3.5.1.5	High-Temperature Process.....	260
3.5.1.6	Chlorination	260

3.5.2	Bastnasite.....	261
3.5.2.1	Processing Bear Lodge Ore	266
3.5.2.2	Goldschmidt Process	266
3.5.3	Xenotime	269
3.5.4	Ion-Adsorption Ore	270
3.5.5	Elliot Lake Uranium Ore	273
3.5.6	Gadolinite	273
3.5.7	Euxenite, Fergusonite, and Samarskite	274
3.5.8	Loparite and Pyrochlore.....	276
3.5.9	Apatite	277
3.6	Separation Processes	279
3.6.1	Selective Oxidation	279
3.6.2	Selective Reduction	281
3.6.3	Fractional Crystallization.....	282
3.6.4	Fractional Precipitation	283
3.6.5	Ion Exchange	285
3.6.5.1	Method	285
3.6.5.2	Application.....	287
3.6.6	Solvent Extraction	290
3.6.6.1	Method.....	290
3.6.6.2	Organophosphorus Acids.....	293
3.6.6.3	Carboxylic Acids	300
3.6.6.4	Solvating Extractants	301
3.6.6.5	Amines.....	303
3.6.6.6	Synergistic Effects	306
3.6.6.7	Industrial Processes	307
3.6.6.8	Molycorp.....	308
3.6.6.9	Denison Mines.....	309
3.6.6.10	Indian Rare Earths.....	310
3.6.6.11	Mintek.....	318
3.6.6.12	Megon	319
3.6.6.13	Rhône-Poulenc.....	321
3.6.6.14	Thorium Ltd.....	322
3.6.6.15	Yao Lung Chemical Plant.....	322
3.6.6.16	Spin-Off Processes	327
3.6.6.17	Dry Processes	328
3.7	Scandium	329
3.8	Summary	330
Chapter 4	Reduction.....	333
4.1	Introduction	333
4.2	Fundamentals	333
4.3	Metallotherapy	337
4.4	Preparation of Rare-Earth Chlorides	339

4.4.1	Preparation of Hydrated Rare-Earth Chlorides	339
4.4.2	Dehydration of Hydrated Rare-Earth Chlorides	339
4.4.3	Dry Methods	345
4.4.4	Purification of Rare-Earth Chlorides	346
4.5	Reduction of Rare-Earth Chlorides.....	348
4.5.1	Early Attempts.....	348
4.5.2	Reduction in a Refractory Bomb.....	350
4.5.3	Reduction in a Tantalum Crucible.....	352
4.5.4	Intermediate Alloy Processes.....	353
4.5.5	Kroll-Type Processes.....	353
4.5.5.1	Lithium/Sodium Reduction of Yttrium Chloride	353
4.5.5.2	Lithium Reduction of Yttrium Chloride ...	355
4.5.5.3	Lithium Reduction of Rare-Earth Chlorides.....	357
4.5.5.4	Lithium Reduction of Dysprosium, Holmium, and Erbium Chlorides	358
4.6	Preparation of Rare-Earth Fluorides	363
4.6.1	Wet Method	363
4.6.2	Dry Methods	364
4.6.2.1	Reaction of Rare-Earth Oxides with Anhydrous HF	364
4.6.2.2	Reaction of Rare-Earth Oxides with Ammonium Bifluoride.....	366
4.6.3	Purification of Rare-Earth Fluorides	367
4.7	Reduction of Rare-Earth Fluorides	368
4.7.1	Lithium Reduction.....	369
4.7.2	Calcium Reduction (Ames Process).....	371
4.7.2.1	Semicontinuous Reduction	372
4.7.2.2	Goldschmidt Process	374
4.7.3	Intermediate Alloy Process	376
4.7.4	Preparation of Scandium	379
4.7.5	Reduction of Samarium, Europium, and Ytterbium Halides.....	379
4.7.5.1	Reduction of SmCl_3 by Mechanical Milling	380
4.8	Oxide Reduction Processes	380
4.8.1	Reduction–Distillation: Lanthanothermy	382
4.8.1.1	Preparation of Samarium and Ytterbium ...	383
4.8.1.2	Preparation of Europium	383
4.8.1.3	Preparation of Samarium, Europium, Ytterbium, and Terbium.....	384
4.8.2	Reduction–Distillation: Other Reductants	386
4.9	New Reduction Procedures	397
4.9.1	Metallothermic Reduction in Molten Salt.....	398

4.10	Carbothermic Reduction	401
4.11	Electrolytic Production of Rare-Earth Metals	402
4.11.1	Chloride Electrolysis	403
4.11.2	Electrowinning at Room Temperature	408
4.11.3	Electrowinning Solid Metal Deposits	409
4.11.4	<i>In Situ</i> Preparation of Electrolyte.....	409
4.11.5	Commercial Electrowinning from Rare-Earth Chlorides	410
4.11.6	Oxide–Fluoride Electrolysis.....	411
4.11.6.1	Gray’s Cell	412
4.11.6.2	Reno Cell Type 6	413
4.11.6.3	Reno Cell Type 12	415
4.11.6.4	Reno Continuous Cell Type 12	418
4.11.6.5	Cells for Electrowinning Lanthanum	419
4.11.6.6	Cell for Electrowinning Neodymium, Praseodymium, and Didymium.....	426
4.11.6.7	High-Temperature Electrowinning Cell ...	428
4.12	Recovery of Rare-Earth Metals as Alloys.....	431
4.12.1	Electrolysis of Chlorides	432
4.12.2	Electrolysis of Oxide–Fluoride Melts	435
4.12.2.1	Electrodeposition of Europium from Molten Fluoride	441
4.12.2.2	Electrochemical Reduction of Cerium Oxide to Metal.....	441
4.13	Current Efficiency	442
4.14	Summary	442
Chapter 5	Refining	447
5.1	Introduction	447
5.2	Origin of Impurities.....	448
5.2.1	Starting Materials.....	449
5.2.2	Crucible	451
5.2.3	Environment	452
5.3	Methods for Impurity Removal	453
5.4	Pyrovacuum Treatments	453
5.4.1	Distillation.....	454
5.4.2	Removal of Halogens/Halides.....	455
5.4.3	Degassing	457
5.4.3.1	Dehydrogenation.....	457
5.4.3.2	Denitrogenation	457
5.4.3.3	Deoxidation.....	458
5.4.3.4	Sacrificial Deoxidation	458
5.4.3.5	Carbon Deoxidation.....	460
5.4.3.6	Silicon Deoxidation	461
5.5	Pyrovacuum Techniques.....	462

5.5.1	Lanthanum, Cerium, Praseodymium, and Neodymium.....	463
5.5.2	Yttrium, Gadolinium, Terbium, and Lutetium	463
5.5.3	Scandium, Dysprosium, Holmium, Erbium, and Lutetium	473
5.5.4	Samarium, Europium, Thulium, and Ytterbium	475
5.5.4.1	Purification of Europium by Distillation....	475
5.6	Electrorefining	478
5.6.1	Yttrium	478
5.6.2	Gadolinium.....	482
5.6.3	Cerium.....	489
5.7	Ultrapurification Methods	490
5.8	Zone Refining	490
5.8.1	Preliminary Studies.....	491
5.8.2	Lanthanum, Gadolinium, and Terbium	493
5.8.3	Lanthanum, Cerium, and Gadolinium	493
5.8.3.1	Redistribution of Interstitial Impurities....	496
5.8.3.2	Redistribution of Metallic Impurities	497
5.9	Solid-State Electrotransport	500
5.9.1	SSE System.....	503
5.9.2	Residual Resistivity Ratio	505
5.9.3	Lanthanum	505
5.9.4	Praseodymium.....	505
5.9.5	Neodymium.....	506
5.9.6	Gadolinium.....	506
5.9.7	Terbium.....	506
5.9.8	Yttrium	507
5.9.9	Dysprosium and Holmium	507
5.9.10	Erbium.....	508
5.9.11	Lutetium	509
5.9.12	Samarium	510
5.10	Zone Refining and Electrotransport	510
5.10.1	Neodymium.....	510
5.10.2	Gadolinium.....	512
5.11	Iodide Refining	515
5.12	Miscellaneous Processes	515
5.12.1	Deoxidation by Oxyhalide Formation.....	516
5.12.2	Electrochemical Deoxidation of Rare-Earth Metals....	517
5.13	Summary	520
Chapter 6	Rare-Earth Materials.....	523
6.1	Introduction	523
6.2	Misch Metal.....	523
6.2.1	Preparation of Mixed Rare-Earth Chlorides.....	524
6.2.2	Electrolysis of Chlorides	526

6.2.3	Electrolysis of Oxide–Fluoride Melts	528
6.2.4	Ames Process	532
6.2.5	Thermal Reduction Process	534
6.3	Rare Earth–Silicon–Iron Alloys	538
6.3.1	Reno (USBM) Process	538
6.3.2	BARC Process	541
6.3.3	Baotou Process	541
6.4	Rare Earth–Magnesium–Silicon Alloys	541
6.5	Rare Earth–Aluminum–Zinc Alloys	543
6.6	Yttrium–Aluminum Alloys	544
6.7	RE–TM–Mg Alloys	545
6.8	FCC Catalysts	545
6.9	Permanent Magnet Materials	546
6.10	Rare Earth–Co Permanent Magnets	546
6.10.1	Preparation of Magnet Material	549
6.10.1.1	Direct Melting	550
6.10.1.2	Reduction–Diffusion	550
6.10.1.3	Coredreduction	555
6.10.1.4	Electrolysis	556
6.10.2	Preparation of Magnets	561
6.10.2.1	Sintered Magnets	562
6.10.2.2	Precipitation–Hardened Magnets	564
6.10.2.3	Bonded Magnets	565
6.11	Neodymium–Iron–Boron Magnets	567
6.11.1	Production of Nd–Fe–B Alloys	568
6.11.1.1	Direct Melting	568
6.11.1.2	Coredreduction	568
6.11.1.3	Production of Consolidated Alloys	569
6.11.2	Production of Nd–Fe–B Magnets	575
6.11.2.1	Melt Spinning	576
6.11.2.2	Strip Casting	577
6.11.2.3	Hydrogenation–Disproportionation– Desorption–Recombination	577
6.11.2.4	Consolidation	580
6.11.2.5	Sintered Magnets	586
6.11.3	Preservation and Enhancement of Magnetic Properties	589
6.11.3.1	Super High-Energy Magnets	592
6.11.3.2	Two-Alloy Process	594
6.11.4	Corrosion Control by Coatings on Magnets	595
6.12	Sm–Fe–N Magnets	598
6.13	Lanthanum Substitution in Ferrites	599
6.14	Magnetostrictive Material (Terfenol-D)	601
6.15	Magnetic Refrigerants (Magnetocaloric Materials)	602
6.15.1	Magnetic Refrigeration	603
6.16	Thin Film Deposition Processes	605

6.16.1	Bubble Domain Memory Materials	606
6.16.2	Magneto-Optic Storage Media.....	606
6.17	NiMH Battery and Hydrogen Storage Materials.....	607
6.17.1	LaNi ₅ –Hydrogen System.....	607
6.17.2	Preparation of the Alloys	607
6.17.3	Alloys for Hydride Compressor	609
6.17.4	Preparation of Multicomponent RE–Ni–Mg Intermetallics.....	609
6.18	Special Rare-Earth Ceramics	610
6.18.1	Yttrium Aluminum Garnet, Nd:YAG Ceramics.....	610
6.18.2	Gadolinium Gallium Garnet	611
6.18.3	Scandia Ceramics	611
6.18.4	Rare-Earth Sulfides	612
6.19	Preparation of Rare-Earth Phosphors.....	612
6.19.1	Homogeneous Precipitation.....	612
6.19.2	Solid-State Reaction	614
6.19.3	Sol-Gel Synthesis	615
6.19.4	Melt Synthesis	616
6.19.4.1	Molten Salt Synthesis	616
6.19.4.2	Flux Method	617
6.20	Superconductors	617
6.21	Summary	621
Chapter 7	Recycling.....	627
7.1	Introduction	627
7.2	Materials for Recycling	636
7.3	Potential for Recycling	637
7.4	Processes for Recycling.....	640
7.5	Pyrometallurgical Processes	640
7.5.1	Smelting.....	640
7.5.2	Melt Spinning.....	643
7.5.3	Chlorination.....	645
7.5.4	Chemical Vapor Transport	646
7.5.5	Liquid Metal Extraction	646
7.5.5.1	Ames Process.....	647
7.5.6	Flux-Based Processes	649
7.5.6.1	Electroslag Refining	649
7.5.6.2	Molten Flux Process	650
7.5.6.3	Glass-Slag Method.....	650
7.5.7	Oxidation–Reduction and Other Options.....	651
7.6	Hydrometallurgy	652
7.6.1	Leaching and Precipitation.....	653
7.6.1.1	Rhône Poulenc Process.....	656
7.6.1.2	Hydrothermal Process	658
7.6.2	Leaching, Precipitation, Solvent Extraction.....	658

7.7	Separation of Individual Rare Earths	664
7.8	Magnets	668
7.8.1	In-Plant or Preconsumer Scrap	669
7.8.2	End-of-Life Scrap	669
7.8.2.1	Collection	669
7.8.2.2	Dismantling	670
7.8.2.3	Samarium–Cobalt	671
7.8.2.4	NdFeB	671
7.8.2.5	Mixed Sm–Co and Nd–Fe–B Scrap	671
7.9	Nickel–Metal Hydride Batteries	672
7.10	Phosphors	672
7.10.1	Composition of Recycled Lamp Phosphor	673
7.10.2	Physical Separation	675
7.10.3	Separation of Individual Phosphors	676
7.11	Glass-Polishing Powder	682
7.12	Catalysts	683
7.12.1	Fluid Cracking Catalysts	683
7.12.2	Automotive Exhaust Catalysts	684
7.13	Optical Glass	684
7.14	Miscellaneous Materials	685
7.15	Summary	685
Chapter 8	Analysis	687
8.1	Introduction	687
8.2	Chemical Methods	687
8.2.1	Gravimetry	687
8.2.2	Volumetry	688
8.2.2.1	Determination of Cerium	688
8.2.2.2	Determination of Europium	689
8.3	Analytical Separation of Rare Earths	689
8.4	Instrumental Methods	689
8.5	Spectroscopy	690
8.5.1	Spectrophotometry	690
8.5.2	Emission and Absorption Spectroscopy	693
8.5.3	Induction-Coupled Plasma Excitation	698
8.5.4	ICP-AES	698
8.6	ICP-MS	700
8.7	XRF	703
8.8	NAA	705
8.9	Other Instrumental Techniques	710
8.9.1	Cathode Ray–Excited Emission Spectroscopy	710
8.9.2	X-Ray–Excited Optical Luminescence Spectroscopy	710
8.9.3	Spark Source Mass Spectrometry	711
8.9.4	Secondary Ion Mass Spectrometry	711

8.10	Determination of Interstitials	711
8.11	Summary	713
Chapter 9	Environmental Aspects	717
9.1	Introduction	717
9.2	Contaminant Elements in Rare-Earth Ores	718
9.2.1	Radioactive Contaminants	718
9.2.2	Contaminants from Hard-Rock Mining.....	719
9.2.3	Rare-Earth Elements	720
9.3	Main Process Steps in Mining and Processing	720
9.4	Contaminant Release Points	721
9.4.1	Mine Pit	723
9.4.2	Tailing Impoundment.....	723
9.4.3	Waste Rock Stockpiles	724
9.4.4	Mill	724
9.4.5	Air Emissions	724
9.4.6	Mine Site	724
9.4.7	Head-End Processing	725
9.5	Environmental Aspects of Mining and Processing in China.....	725
9.5.1	Overview	725
9.5.2	Bayan Obo Facilities	726
9.5.3	Sichuan Mine.....	726
9.5.4	Ion-Adsorption Deposits	727
9.5.5	Processing	727
9.5.6	Wastewater from REE Separation and Refining	727
9.6	Entry Criteria for Rare-Earth Industry (China)	730
9.7	Research and Development on Cleaner Production in China.....	731
9.7.1	Technology Solutions to Environmental Problems.....	731
9.7.1.1	Fluorine Emission and Mitigation	731
9.7.1.2	Eco-Friendly RE/Th Separation.....	732
9.7.1.3	Wastewater Treatment	732
9.8	Environment-Friendly Processing outside China.....	734
9.8.1	General Outlook	734
9.8.1.1	Monazite and Xenotime.....	734
9.8.2	Recovery Rates.....	734
9.8.3	Mine Planning and Management	735
9.9	Mountain Pass	735
9.10	Bear Lodge	738
9.10.1	Water Contamination	738
9.10.2	Air Contamination	739
9.11	Mount Weld	739
9.12	Dubbo Zirconia Project	740

9.13	Kvanefjeld.....	741
9.14	Steenkampskrall Mine	742
9.15	Nechalacho Project.....	742
9.16	Summary	743
References		745

Preface to the Second Edition

At the time of writing the Preface to the first edition, we realized and also wrote that the future of rare earths would be glorious and full of excitement, be it in science, technology, or commercial utilization. Subsequent events more than confirmed these expectations, and the rare earths have also become widely popular in the sense that a person on the street anywhere in the world knows that rare earths are useful and they are important. Thanks to the Internet, we could also evaluate who used the book and how the book we wrote was used. The readership profile that emerged helped in casting the second edition.

In the 10 years that have passed since the publication of the first edition of *Extractive Metallurgy of Rare Earths*, we realized that developments in the field pertained more to rare-earth materials processing (converting a rare-earth metal, alloy, or compound to a device-ready material) than to materials preparation (converting an ore or a concentrate to a sufficiently pure rare-earth metal, alloy, or compound). In fact, the basic knowledge structure on materials preparation was built and reached maturity in the period we covered in the first edition. Efforts continued and some interesting breakthroughs were achieved in the past 10 years, too, in the challenging area of rare-earth separation. On the whole, the requirement in the area of materials preparation (the essence of extractive metallurgy) at the present time is to translate the technically feasible processes into commercially viable processes. This needs to be done not only for the well-known and well-studied resource minerals monazite, bastnasite, and xenotime but also for numerous other minerals that pose challenges by the nature of their dissemination (especially extremely fine-grained occurrences) and complexity of their compositions in addition to low rare-earth concentrations.

Commercial viability has a new dimension now—community acceptability. For some time in the past and possibly forever in the future, the implementation of any extractive metallurgy process in a plant is possible only in a regime of strict regulations with liberal safety margins. This translates to minimization of energy consumption (direct and indirect), chemicals, and water, and minimization or elimination of liquid or gaseous effluents and solid waste. The regulations as regards radioactive materials (uranium, thorium, and their natural decay products) are stricter. Even the very processing of monazite is not allowed in Australia and China. These requirements are attempted to be implemented by various process and plant design innovations and suitable plant practices. As regards extractive metallurgy and rare earths, the focus of recent research efforts has been in trying out new reagents and processes, particularly for rare-earth separations. Regulatory changes have been outlined even in the metal and alloy production processes, which, in the case of rare earths, are not known to be particularly *polluting*. For the electrolytic production of misch metal, chloride electrolytes are not allowed in certain countries. Current and future rare-earth extractive processes need to be in tune with these parameters. The process metallurgy *per se* presented in this edition keeps this background in view.

The rare-earth industry has been through a strange transformation. Time and again it has been noted that rare earths are abundant, and deposits of rare earths

are widely distributed throughout the world. Major consumers (Japan, EU) never had large deposits in their own geographical boundaries but nevertheless had access to large deposits with fairly high reliability. The United States, Australia, China, and India needed the rare earths and also had deposits in their own boundaries. By the mid- and late 1980s, it was also clear that rare earths are vital and largely without substitute for all important technology devices including those for *green* electric power generation, lighting, and surface transportation, apart from military hardware. Yet, instead of a natural proliferation of mining and production facilities all over the world, the technology activities moved to China, and a decade and a half later, all stakeholders realized that this was not a sustainable arrangement. Then followed a flurry of activities to identify and develop new mines and production facilities. This has been the liveliest area of rare-earth extractive metallurgy. It has been extensively covered in this edition.

Limited natural availability of certain key rare-earth elements like Dy and Eu, general uncertainty in the continued availability of these and other elements from primary sources at a reasonable cost, and regulatory pressures on industrial procedures for primary rare-earth production have steadily contributed to the emergence of recycling as an important process option for the rare earths. Recycling as a materials supply route comes with a host of advantages that concerns economy, environment, reliability, energy, and ethics. There are also challenges to overcome, both relating to logistics to ensure accessibility of recyclable material, and process to ensure maximum retention of the value addition that occurred in primary processing. A new chapter on recycling addresses various issues in the recycling of rare earths—the advantages and limitations, and the methods used worldwide to manage them.

Precise quantification of the rare earths in various materials, be they ores, concentrates, and such starting materials, interprocess intermediates, as well as products such as metals, alloys, and compounds, is essential for the development of extractive processes for the rare earths. Depending on the matrix, co-occurring elements, and the relative concentration of various components, a number of analysis techniques have been developed and fine-tuned for the rare earths. Classical chemical methods, instrumental techniques based on absorption and emission of radiation, charge-to-mass ratio of the constituent nuclides, as well as propensity to radioactivation and the nature of radioactivity formed have all been used in the analysis of rare earths at various concentration levels—from a tenth of a ppm to tens of percent. Rare earths as a group as well as individual rare earth elements have been determined in rare-earth and non-rare-earth matrices. Non-rare-earth impurities have been determined in rare-earth matrices. All techniques relevant to extractive metallurgy of rare earths have been covered in the new chapter on analysis.

Apart from the scientific merit and engineering elegance of a flow sheet for rare-earth extraction and processing, including mining and beneficiation, that the scheme will become plant practice or would remain as one depends strongly on its environmental impact. The land, water, and energy use and plant emissions into the atmosphere, and types and quantities of liquid effluents and solid wastes, their storage, and disaster potential are all factors that determine the siting and continued existence of a rare-earth facility. It is becoming increasingly important that if the rare

earths are for green energy, their mining, extraction, and processing must also meet green standards. The new chapter on environmental aspects deals with such issues.

All features of the first edition that the authors perceived to be useful to readers have been retained in this edition as well, and new materials, as outlined above, have been added. We have made liberal (hundreds of them) use of tables and figures and accommodated varied approaches to solving current and potential issues in rare-earth technology. We wanted to reveal research gaps and areas that would benefit from further work. We expect the book to be useful to a broad spectrum of people spanning academic, research, and industrial backgrounds related in any way to rare-earth technology.

The idea of a second edition was mooted by Allison Shatkin, senior editor, Books, Materials Science & Chemical Engineering, Taylor & Francis, and has become a reality entirely because of her strong support. Amber Donley was tremendously helpful and supportive during the long process of manuscript preparation and publication, and so were Iris Fahrer and Adel Rosario in transforming the manuscript to the final book. Kizza Florence, Arlene Kopeloff, and Jennifer Ahringer of CRC Press helped with the development of the book at various stages. We are deeply grateful to them.

Steve Constantinides and Doris Schuler graciously permitted liberal use of material from their publications and presentations. Elsevier kindly accorded permission to use a remarkable number of tables and figures. The institutional support from Bhabha Atomic Research Centre, the publications of the US Geological Survey and Technology Metals Research have been invaluable resources for this book. In a way, we stood on the shoulders of such giants to create this work.

Yatin Thakur at BARC has been a trusted teammate in our authorship endeavor. He skillfully prepared the line drawings for the first edition and also the additional figures for the second edition.

We warmly acknowledge the support of our family members. I (NK) thank my wife Kusuma (a banker) and daughter Kavita (a civil engineer) for their time, support, and constant encouragement during the preparation of the manuscript, especially when the going got tougher and hours spent endless.

**Nagaiyar Krishnamurthy
Chiranjib Kumar Gupta**

Preface to the First Edition

A chronological account of the chemistry and metallurgy of the rare earths is arranged into three eras or ages. The basis of this division is the availability and purity of the rare-earth metals and materials and the scientific and engineering information about them. The period prior to 1950 may be called the *Dark Age*. The next two decades were the *Age of Enlightenment*. The period after the early 1970s may be considered the *Golden Age*. In the first three decades of this golden era, a number of remarkable advances and discoveries were made in the field of rare earths, and these have left an indelible mark on the global materials scenario. It is widely perceived that the future of the rare earths will be glorious and full of excitement, be it in science, technology, or commercial utilization.

The rare earths are a community of 17 metallic elements, all but one occurring naturally (14 lanthanides and 2 associated elements). They are found in combination in mineral deposits widespread throughout the world. Notably large reserves exist in China, the United States, and Australia. The word *rare* in *rare earths* arises more from the historical difficulty in separating and obtaining them as individual pure elements than from their inherent nonavailability. There have been major developments in the technologies for the production of separated high-purity rare earths. Highly efficient separation technologies have been key to the exploitation of the rare earths in a wide range of now commonplace applications that have slowly become an inseparable part of modern living.

At the Bhabha Atomic Research Centre in Mumbai, India we had a long, direct, and active association with rare-earth research and production practices. That has been the motivation to write, in 1992 an extensive review on the extractive metallurgy of the rare earths. This was published in the *International Materials Reviews*. With the publication of the review in 1992, its enthusiastic reception, and our progressively increasing involvement with the rare earths, we attempted to preserve the available information on the extractive metallurgy of the rare earths in the form of a book. This thinking gathered further momentum because we found that although a voluminous literature in the form of numerous conference proceedings, a highly rated series of volumes on the physics and chemistry of the rare-earth elements (edited by Gschneidner and Eyring), and important trade publications and newsletters is available, all of these publications have objectives different from that of our book. We are not aware of any other text that covers the subject in the manner we have attempted here. We have worked to bring together all relevant matters concerning the extractive metallurgy of the rare earths and related information that, at present, remains scattered in a variety of forms of published literature.

This book has been organized into seven chapters. Chapter 1, The Rare Earths, provides the background information on the properties and applications of the rare earths and highlights the links of these aspects to the totality of rare-earth extraction and processing techniques. The interesting sequence of the discovery of the rare earths is first presented, followed by a listing and discussion of the currently accepted

values and information pertaining to the various properties of the rare earths. A comprehensive account of all major applications of the rare earths is then provided.

Chapter 2, Resources, presents in detail all currently available information on the world's rare earth resources, their location, quality, and quantity. The resource utilization trends and patterns from the times when the rare earths were first produced as a commodity up to the present are presented. Factors leading to the unequal availability of the rare earths are highlighted, and the world's rare earth resources position is dealt with in the context of current and projected demands.

Chapter 3, Resource Processing, incorporates a detailed account of the techniques for the processing of the various rare earth resources and the separation of individual rare earth elements. While placing a strong emphasis on the modern methods of solvent extraction and ion exchange, the salient features of the classical methods of rare earth separation are covered in detail. Various options for the treatment of the as-mined rare earth resources by physical and chemical beneficiation methods prior to separation are discussed.

Chapter 4, Reduction, deals with the techniques for converting the pure rare earth oxide intermediates to the metals. The numerous scientifically interesting and technologically challenging procedures for rare earth metal reduction are described in considerable detail. Chemical as well as electrochemical reduction methods have been used and the variety in the actual processes has come about because of the different physical properties of the individual rare earth elements. Particularly, the melting and boiling points of the elements dictate the type of process best suited for reduction. These aspects are discussed.

Chapter 5, Refining, is devoted to the purification of the rare earth metals. Elucidation of the unique properties of the rare earth elements has been possible only with the availability of these elements in very pure forms; therefore, major efforts have gone into the development of suitable techniques such as pyrovacuum treatment, zone melting, and electrotransport to prepare metals of high purity levels. The chapter covers these refining techniques as applied to different rare earth metals.

Chapter 6, Rare-Earth Materials, is concerned with the techniques for the preparation of the numerous rare earth alloys and compounds and rare earth bearing materials. Among the materials described are the traditional products like misch metal and rare earth-iron-silicon alloys, as well as new materials like lanthanum-nickel alloys, permanent magnet materials based on samarium and neodymium, magnetostrictive and magnetocaloric materials. The procedures followed by various manufacturers of rare earth materials are outlined. The presentation also covers methods under investigation for newer materials.

Chapter 7 is an overview—a sojourn for the reader in the world of the rare earths. While going through this chapter one can develop a brief but significant acquaintance with the rare earths in their entirety.

In all the chapters, the text is liberally supported by tables and figures. Key property values and results have been listed in the tables, and the figures comprise line drawings of equipment and flow sheets of processes. References to original papers are extensively made in the text and all the references are grouped in one place at the

end of the book. The reference list will serve as a very useful guide for those who want to refer to the original sources for more information on specifics.

We hope this book will be useful to professionals involved with the extraction, separation, concentration, and production of the rare earth metals, alloys, and chemicals. They include process, production, and regulatory staff engineers; management as well as research and development professionals; graduate students; and libraries attached to universities and R&D establishments.

We would like particularly mention the contributions of certain people who have been especially involved, with the preparation of this book. The work pertaining to the production of the typed version of the manuscript in its finished form was very efficiently handled by Poonam Khattar. All figures for the book were drawn by Yatin Thakur. We are grateful to the editorial department of G+B, particularly to Catherine Bewick in the initial stages and to Sally Cheney, Lloyd W. Black, and Matt Uhler in the latter stages for supporting and encouraging us in the project.

Finally, we wish to dedicate this book to our wives, Chandrima Gupta and Kusuma Krishnamurthy, in gratitude for their unique contributions toward the completion of this work.

Chiranjib Kumar Gupta

Nagaiyar Krishnamurthy

Bhabha Atomic Research Centre, Mumbai, India

Authors

Dr. Nagaiyar Krishnamurthy was affiliated with the Materials Group, Bhabha Atomic Research Centre (BARC), Mumbai, India for nearly four decades, conducting and later formulating and guiding research in the extraction and processing of rare earths, reactive and refractory metals, and special less common materials.

He earned his BSc degree at the University of Madras in 1974, his MSc in 1980, and his PhD in 1992, both at the University of Bombay. His PhD dissertation was on the pyrometallurgy of group V refractory metals and their alloys with group IV metals.

He is a professor at the Homi Bhabha National Institute and has guided many students to complete their PhD. He has been a member of Indian Rare Earths Technology Development Council. In addition to the more than 100 original research papers published in peer-reviewed international journals, Dr. Krishnamurthy coauthored the first edition of *Extractive Metallurgy of Rare Earths* published by CRC in 2004. Earlier he coauthored the book *Extractive Metallurgy of Vanadium* published by Elsevier in 1991 and a monograph on the Binary Phase Diagrams of Tantalum published in 1996 by the Indian Institute of Metals.

Dr. Chiranjib Kumar Gupta retired as the director of the Materials Group, Bhabha Atomic Research Centre (BARC), Mumbai, India in January 2000 after decades of association with BARC. He was instrumental in formulating and directing the programs of the Materials Group in the areas of extraction and processing of refractory metals and materials. He pioneered the open aluminothermic reduction as a process of metal- and alloy-making and contributed extensively to the use of fused salt electrolysis for the preparation and refining of group V and VI refractory metals. He is an alumnus of Banaras Hindu University and guided numerous students to PhD in Mumbai University. Dr. Gupta has authored nearly 200 publications including half a dozen books on nuclear energy and refractory metals. He has been a recipient of numerous awards and honors.

1 The Rare Earths

1.1 INTRODUCTION

The term *rare earths* denotes the group of 17 chemically similar metallic elements that includes scandium, yttrium, and the lanthanides (Spedding 1978; Connelly et al. 2005). The lanthanides are the series of elements with atomic numbers 57 to 71, all of which, except promethium, occur in nature. The rare-earth elements, being chemically similar to one another, invariably occur together in minerals and behave as a single chemical entity. Thus, the discovery of the rare earths themselves occurred over a period of nearly 160 years, from 1787 to 1941 (Szabadvary 1988; Weeks 1956). The problem of separating them from one another for scientific study or industrial use then followed. This has been one of the most challenging tasks of rare-earth technology. While the attempts to separate the rare earths began with the work of Mosander during 1839–1841, much of the effort directed to the separation of various rare earths occurred from 1891 to 1940. During this period, from the available mixed and separated compound intermediates, many rare-earth alloys and metals were prepared, and commercial applications were developed for mixed or roughly separated rare earths. The following two decades, 1940–1960, were the most productive in terms of effective process development. Most important were the development of modern separation methods, which resulted in the availability of sufficient quantities of pure individual rare-earth compounds (Powell and Spedding 1959b) for the investigation of reduction processes to prepare pure metals and alloys (Beaudry and Gschneidner 1978) and evaluation of their properties. Beginning in the 1960s, much progress was made in the large-scale production of purer rare earths, in the identification of newer properties, and in their use in a variety of important commercial applications. The usable forms of rare earths encompass naturally occurring oxide mixtures and products synthesized from them, high-purity individual metals, alloys, and compounds. The current annual demand for rare earths is in the range of 125,000 t calculated as rare-earth oxides. The world rare-earth reserves are large and sufficient to support the present level of consumption for many centuries to come.

This chapter is a survey of the history, properties, and applications of the rare earths and highlights the background to their current status as materials of interest in the laboratory and products of use in technology and industry.

1.2 DISCOVERY

The discovery of rare-earth elements began in 1787 and went on for about 160 years to conclude in the 1940s (Szabadvary 1988; Weeks 1956). All the naturally occurring rare earths and all but one of all the rare-earth elements had been discovered by the first decade of the twentieth century, and the discovery of the remaining one rare earth had to wait until the discovery of nuclear reactions.

The rare-earth elements and their discoverers are listed in Table 1.1 and charted in Figure 1.1. The activity started at Ytterby, a village near Stockholm in Sweden. Ytterby was the site of a quarry that had been the source of many unusual minerals containing rare earths.

In 1787, Carl Axel Arrhenius, a lieutenant in the Swedish Royal Army and also an amateur mineralogist, found a black mineral, until then not mentioned by anyone, in Ytterby. The mineral was analyzed by the Finnish chemist Johan Gadolin in 1794. Gadolin found iron and silicate as constituents of the mineral and also a “new earth,” which accounted for 30% of the mineral. The discovery of the new earth by Gadolin was confirmed by the Swedish chemist Anders Gustaf Ekeberg the following year. Ekeberg found that the mineral also contained beryllium, a metal that had been recently discovered by the French chemist Nicolas Louis Vanquelin. The mineral found by Arrhenius turned out to be an iron–beryllium–silicate. Ekeberg gave the name *yttria* to the new earth discovered by Gadolin and also named the mineral *gadolinite*.

Until the first decade of the nineteenth century, “earths” were universally considered to be elements. The fact that earths were not elements but compounds was first stated by the Hungarian chemist Antal Ruprecht but conclusively proved by Sir Humphrey Davy, who electrolyzed melts of earths and obtained metals from them. In the first decade of the nineteenth century, Davy separated numerous metals such as calcium, strontium, and barium from alkaline earths, and from then on, the metals were distinguished from earths. For example, chemists began to use the name *yttrium* for the metal instead of *yttria* even though the metal itself had not been produced in the pure state.

TABLE 1.1
Discovery of the Rare-Earth Elements

Year	Mineral/ Element	Discovered by	Named by	Confirmed by	Origin of Name
1787	Gadolinite	C.A. Arrhenius	A.G. Ekeberg	M. Delafontaine	Person: J. Gadolin
1794	Yttria	J. Gadolin	A.G. Ekeberg		Place: Ytterby
1751	Cerite	A.F. Cronstedt	J.J. Berzelius, W. Hisinger		Asteroid: Ceres
1804	Cerium	J.J. Berzelius, W. Hisinger	J.J. Berszelius, W. Hisinger		Asteroid: Ceres
1839	Samarskite	M.H. Klaproth, G. Rose			Person: Col. Samarsky
1839	Lanthanum	C.G. Mosander	J.J. Berzelius		Chemical behavior: to escape notice
1842	Didymium	C.G. Mosander	C.G. Mosander		Chemical behavior: twins (Continued)

TABLE 1.1 (CONTINUED)**Discovery of the Rare-Earth Elements**

Year	Mineral/ Element	Discovered by	Named by	Confirmed by	Origin of Name
1843	Erbium (known as terbium after 1864)	C.G. Mosander	C.G. Mosander	M. Delafontaine, J.L. Soret, H.E. Roscoe, A.J. Schuster, J.G. Marignac, J.L. Smith	Place: Ytterby
1843	Terbium (known as erbium after 1864)	C.G. Mosander	C.G. Mosander	M. Delafontaine, J.L. Smith	Place: Ytterby
1878	Ytterbium	J.C. Marignac	J.C. Marignac	M. Delafontaine, L.F. Nilson	Chemical behavior: between erbium and yttrium
1879	Samarium	P.E.L. de Boisbaudran	P.E.L. de Boisbaudran	P.T. Cleve	Mineral: samarskite
1879	Scandium	L.F. Nilson	L.F. Nilson		Place: Scandinavia
1879	Thulium	P.T. Cleve	P.T. Cleve		Place: Scandinavia (<i>Thule</i> is her ancient name)
1879	Holmium	P.T. Cleve	P.T. Cleve	J.L. Soret, P.E.L. de Boisbaudran	Place: Stockholm (medieval name)
1886	Dysprosium	P.E.L. de Boisbaudran	P.E.L. de Boisbaudran		Chemical behavior: difficult to access
1886	Gadolinium	J.C. Marignac	J.C. Marignac	M. Delafontaine, J.L. Soret	Person: J. Gadolin
1886	Praseodymium	C.A. von Welsbach	C.A. von Welsbach	A. Bettendorf	Chemical behavior: green twin
1886	Neodymium	C.A. von Welsbach	C.A. von Welsbach	A. Bettendorf	Chemical behavior: new twin
1901	Europium	E. Demarcay	E. Demarcay	G. Urbain	Place: Europe
1907	Lutetium	G. Urbain, C.A. von Welsbach	G. Urbain		Place: Paris (Roman name of Paris)
1947	Promethium	J.A. Marinsky, L.E. Glendenin, C.D. Coryell	J.A. Marinsky, L.E. Glendenin, C.D. Coryell		Legend: Prometheus

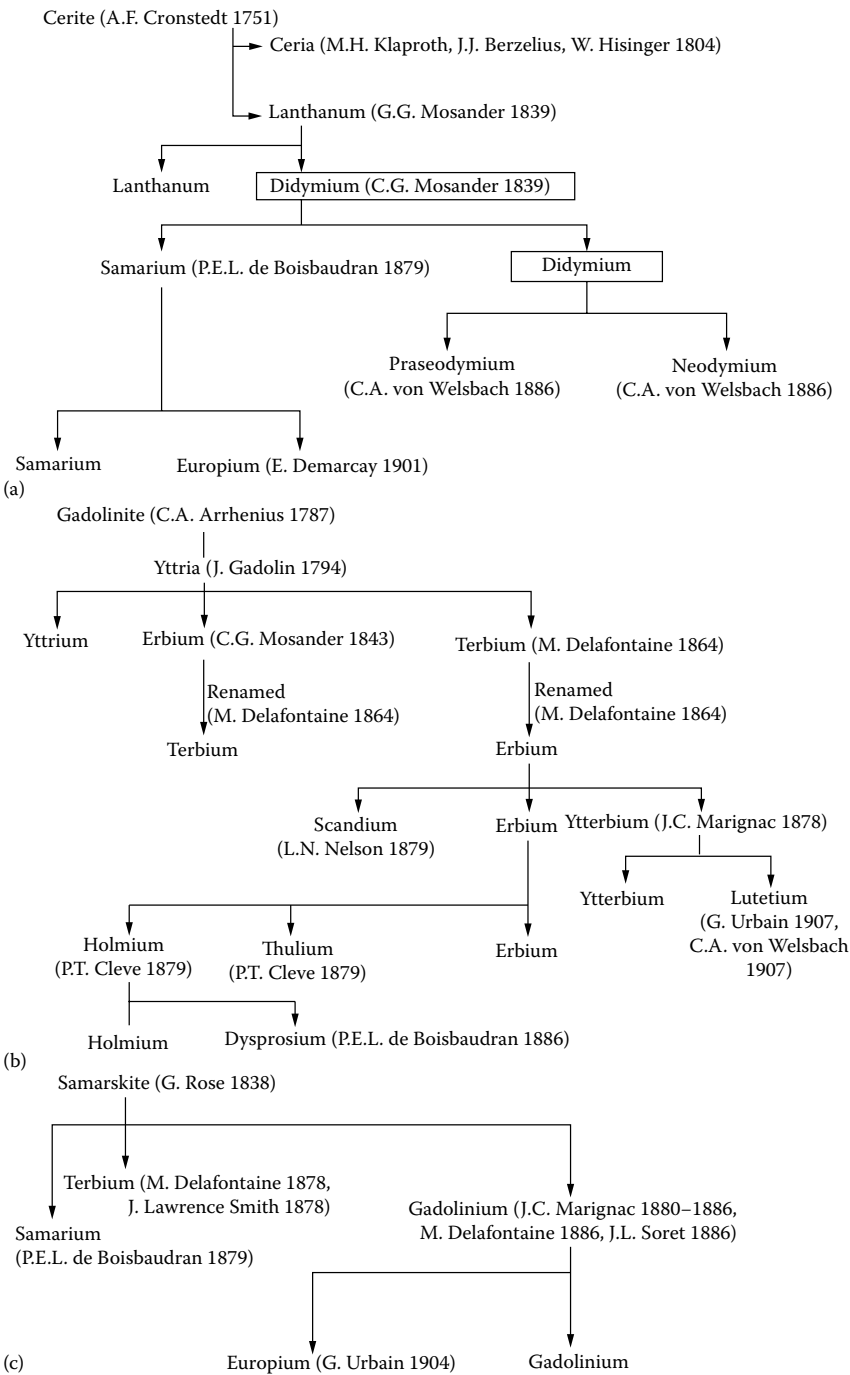


FIGURE 1.1 Discovery of rare-earth elements: (a) cerite sequence, (b) gadolinite sequence, and (c) samarskite sequence.

Interestingly, another new mineral, which was later shown to contain an unknown earth, had been discovered by A.F. Cronstedt in the Bastnäsgrube mine close to Rydderhyatten in Sweden in 1751, before gadolinite was discovered in Ytterby. This mineral was investigated by Jöns Jakob Berzelius and Wilhelm Hisinger in Sweden and independently by Martin Heinrich Klaproth in Germany. They reported simultaneously, in 1804, the discovery of a new element in the mineral. Klaproth was still considering earths as elements and named the new earth *ochroite earth*, while Berzelius and Hisinger stated that the earth was the oxide of a new element. They named the element *cerium* after the asteroid Ceres that had been discovered only 3 years earlier, in 1801. The mineral that contained cerium was named *cerite*.

Carl Gustaf Mosander, an associate of Berzelius, through his patient and painstaking investigations, established that both yttria and ceria were complex in nature and contained new elements. In 1839, Mosander separated a new element from ceria. Berzelius suggested to Mosander the name *lanthanum* for the new element (in Greek, *lanthano* means “to escape notice”). Mosander believed that the lanthanum he separated was not a pure element but might contain yet another new element. Continuing his experiments, he succeeded in 1842 in detecting that new element. He named the new element *didymium*. The element didymium, which was present in cerite, tracked lanthanum in some experiments, while it tracked cerium in some other experiments. It therefore got its name from the Greek word *didymos*, meaning twins, to denote that it accompanied cerium and lanthanum as a twin in the cerium mineral.

The possibility of gadolinite containing new elements in addition to yttrium was already indicated by the works of Heinrich Rose and Berzelius before Mosander turned his attention to this mineral. Reporting his results in 1843, Mosander mentioned not one but two more new elements in gadolinite. He named them *erbium* and *terbium*.

Beginning in the 1850s, a new analytical aid, spectroscopy, was used to identify and confirm the existence of new elements. In 1864, Marc Delafontaine, a Swiss-American chemist, used spectroscopic identification to unequivocally confirm the existence of yttrium, terbium, and erbium. He interchanged, probably unintentionally, the names given by Mosander for terbium and erbium, and the interchanged names have persisted ever since. What was called erbium by Mosander became known as terbium, and what was named terbium by Mosander came to be known as erbium.

There was considerable confusion surrounding terbium and erbium in the 1860s. Delafontaine himself became doubtful, while O. Popp, Johan Fridrik Bahr, and Robert Wilhelm Bunsen denied the existence of terbium while accepting that erbium existed. Charles Augustus Young, an American scientist, demonstrated in 1872 the existence of erbium in the solar spectrum, and the existence of erbium was doubted no more. The matter of terbium was finally resolved by Delafontaine and the Swiss chemist Jean Charles Marignac by 1877–1878. Delafontaine separated the terbium oxide from the mineral *samarskite*, which had been discovered in 1838 by the German mineralogist Gustav Rose. In 1878, J. Lawrence Smith, an American chemist and mineralogist, also reported the existence of terbium in samarskite. In

the same year, Marignac confirmed the presence of terbium in gadolinite, the mineral in which Mosander had originally found the element. Further confirmations of the existence of terbium were provided by the spectral analysis reports of J.L. Soret in 1880 as well as by Sir Henry Enfield Roscoe and A.J. Schuster in 1882.

Delafontaine reported in 1878 that the absorption spectrum of didymium separated from samarskite was not fully identical with the absorption spectrum of didymium separated from cerite. He suspected that didymium was not a single element. Interestingly, in 1879, the French chemist Paul Emile Lecoq de Boisbaudran disproved Delafontaine's report on the spectra but did find a new element in samarskite. He named the element *samarium* after the mineral samarskite in which it was detected.

Investigating gadolinite, Marignac not only had confirmed the existence of terbium in it but also was looking for more new elements in the mineral. He worked on the erbium fraction obtained from the mineral and separated an oxide and salts that were different from erbium in both chemical and spectral characteristics. In 1878, Marignac named the new element *ytterbium* because it stood between yttrium and erbium in its properties. In the same year, Marignac's ytterbium was also identified by Delafontaine in an yttrium niobate mineral called *sipylite*, which had been discovered in Virginia (USA) by John William Mallet in 1877.

The experiments on erbium described by Marignac were repeated in Sweden by Lars Frederick Nilson, and he also confirmed the existence of ytterbium and the statements of Marignac regarding it. Proceeding further, through an exceedingly intricate fractionation procedure, Nilson finally obtained a basic nitrate from gadolinite. He dissolved the salt in nitric acid, and the solution yielded a weak absorption line in the red and in the green spectrum. It also precipitated as an oxalate. Nilson considered this a new element and, in 1879, named it *scandium*, after Scandinavia.

In Sweden, Per Theodor Cleve investigated the erbium fraction remaining after the separation of ytterbium. Based on a spectrum taken by the Swedish physicist Tobias Robert Thalén, Cleve suspected that the erbium fraction could contain more elements. Proceeding with chemical separation and spectral analysis, he identified the existence of two new elements and named them *thulium*, after the legendary old name of Scandinavia, and *holmium*, after the Medieval Latin name of Stockholm. Before Cleve reported his discovery of the new elements in 1879, the Swiss chemist Soret had indicated, on the basis of absorption spectrometry results, the possibility that an unknown element was present in the erbium sample given to him by Marignac. Soret later stated that the unknown element mentioned by him corresponded to Cleve's holmium. The statements and discoveries of Soret and Cleve were confirmed in 1879 by Lecoq de Boisbaudran.

In 1886, Boisbaudran, following an elaborate, intricate, and wearisome method for the chemical separation and spectroscopic and fluorescence studies of rare-earth elements in gadolinite, concluded that the holmium discovered by Cleve contained another new element. He named it *dysprosium*.

Earlier, in 1880, Marignac investigated samarskite by chemical separations. He obtained the nitrate of a substance that differed in many respects from the other elements then known. He tentatively named it $Y\alpha$ and, after more investigations by him as well as by Delafontaine and Soret, in 1886, proposed the name gadolinium for $Y\alpha$.

In 1885, Carl Auer von Welsbach, an Austrian chemist, began investigations on didymium. By then, it was already widely suspected that didymium might not be a single element, but chemical separation efforts to substantiate the presence of the new element were unsuccessful. Auer used fractional crystallization instead of the hitherto applied fractional precipitation to separate didymium. In 1886, he succeeded in obtaining two fractions of didymium ammonium nitrate. He further investigated them by absorption and spark spectrometry and concluded that the fractions belonged to different elements. He named the elements *praseodidymium* and *neodidymium*. In course of time, *di* disappeared from these names, and they came to be known as *praseodymium* and *neodymium*. Mosander's naming of the "element" didymium, meaning twins, was indeed prophetic.

Auer's discovery of praseodymium and neodymium was questioned by Henry Becquerel in 1887, but in 1890 Auer's experiments were repeated by A. Bettendorf, and the existence of praseodymium and neodymium was confirmed. The unseparated mixture of praseodymium and neodymium, however, continued to be referred to by the name didymium.

Samarium, discovered in 1879 in the original didymium by Boisbaudran, was also confirmed as a new element by Cleve. In 1886, the French chemist Eugene Demarcay announced that he separated a new element from samarium. He substantiated his claim only 15 years later in 1901 when he succeeded in preparing it as a pure substance in the form of a double nitrate with magnesium. He named the element *europium*. In 1904, europium was also separated from gadolinium by the French chemist Georges Urbain.

In 1905, Auer mentioned that Marignac's ytterbium probably contained new elements. Two years later, he published experimental results supporting his doubt and stated that ytterbium consisted of two elements. He named them *aldebaranium* and *cassiopeium*. Almost simultaneously, Urbain also reported that ytterbium consisted of two elements, which he named *neoytterbium* and *lutetium*. In the course of time, the names ytterbium (for neoytterbium) and lutetium survived. The name lutetium was derived from the ancient Roman name of Paris.

With the discovery of lutetium, incidentally the last member of the lanthanide series of elements, the story of the discovery of the naturally occurring rare-earth elements, which lasted for well over a century, ended.

Even though all the naturally occurring rare-earth elements had been discovered, the discoverers themselves did not realize that fact. For example, both Auer and Urbain continued to work on reporting new elements. But that was not to be. The theoretical explanation of the great similarity of the properties of the rare-earth elements and also the maximum limit for their number came in later years with the development of the atomic theory. Atomic numbers were introduced by van den Broek in 1912, and Henry Gwyn Jeffreys Moseley discovered, in 1913, a mathematically expressible relationship between the frequency of x-rays emitted by the element serving as an anticathode in the x-ray tube and its atomic number. Urbain subjected all the rare-earth elements discovered in later times to the "Moseley check," to determine their atomic numbers and thus confirm that they were true elements. The range of rare-earth elements, from lanthanum, with atomic number 57, to lutetium, with

atomic number 71, was established. Among these, the element with atomic number 61 was as yet unknown.

In 1941, researchers at the Ohio State University irradiated praseodymium, neodymium, and samarium with neutrons, deuterons, and alpha particles and produced several new radioactivities, which were most probably those of element 61. The formation of element 61 was also claimed in 1942 by Wu and Segre (1942). Chemical proof of the formation of element 61 was provided in 1945 at the Clinton Laboratory (now the Oak Ridge National Laboratory) by Marinsky et al. (1947), who used ion-exchange chromatography to obtain the element from the products of fission of uranium and of neutron bombardment of neodymium. They named the element *promethium* after Prometheus, who stole fire from the Gods for man (Szabadvary 1988). Promethium does not occur in nature.

1.3 SPECIAL CHARACTERISTICS

The close chemical similarity of all the rare-earth elements is, first of all, displayed in their occurring together in nature and further by the fact that it took nearly 160 years of effort by many great names in science to isolate and identify them. It has been borne out by experimental evidence that striking similarities among the chemical properties of the elements and their compounds are the consequence of strikingly similar electronic configurations.

1.3.1 ELECTRONIC CONFIGURATION

The electronic configurations of the rare-earth elements are listed in Table 1.2. Scandium, yttrium, and lanthanum are the elements that begin three successive series of transition elements. Their valence electron configurations are $ns^2(n-1)d^1$, with $n = 4, 5$, and 6 , respectively. They have no f electron. The 14 elements following lanthanum, namely, cerium to lutetium, are the lanthanides (lanthanum-like) and have valence electron configurations represented by $6s^25d^14f^{n-1}$ or $6s^24f^n$. The $5d$ and $4f$ electrons have similar energies in the neutral rare-earth atoms, and this is the reason for two typical electronic configurations. The 14 elements from cerium to lutetium form the series known as the *inner transition* elements or f elements. It must, however, be stated that the electronic configurations given are not known with complete certainty, because of the great complexity of the electronic spectra of these atoms and the consequent difficulty in analysis.

The ionization potentials of rare-earth elements are comparatively low. The elements are therefore highly electropositive and form compounds that are essentially ionic in nature. While all the rare earths form M^{3+} , some of them also occur in +2 and +4 states. These states are always less stable than the +3 state. The occurrence of +2 and +4 states in certain rare earths, which is of considerable importance in rare-earth extractive metallurgy, is related to their electronic structures and ionization potentials. Special stability is apparently associated with empty, half-filled, and filled f shell configurations.

The rare earths scandium, yttrium, and lanthanum form only the M^{3+} ions because this results in the inert gas configuration. Lutetium and gadolinium form only the

TABLE 1.2
Properties of Rare-Earth Elements

Properties	Scandium	Yttrium	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium
Atomic Properties									
Atomic number	21	39	57	58	59	60	61	62	63
Atomic weight	44.95591	88.90585	138.9055	140.115	140.90765	144.24	(145)	150.36	151.965
Crystal structure	cph < 1337;	cph < 1478;	deph < 1478;	fee < -148;	deph < 795;	deph < 863;	deph < 890;	rhomb <	bcc
	bcc > 1337	bcc < 1478	fcc > 310	deph > 148	bcc > 795	bcc > 863	bcc > 890	734;	
			and < 865;	and < 139;				cph > 734	
			bcc > 865	fcc > 139				and < 922;	
				and < 726;				bcc > 922	
				bcc > 726					
Atomic volume, cm ³ /mol at 24°C	15.059	19.893	22.602	17.2	20.803	20.583	20.24	20.000	28.979
Density, g/cm ³ at 24°C	2.989	4.469	6.146	8.16	6.773	7.008	7.264	7.520	5.244
Conduction electrons	3	3	3	3, 3.1	3	3	3	3	2
Valence in aqueous solution	3	3	3	3, 4	3	3	3	3, 2	3, 2
Color in aqueous solution, RE ³⁺	Colorless	Colorless	Colorless	Colorless	Yellow-green	Rose	Pink	Yellow; Sm ²⁺ is deep red	Colorless; Eu ²⁺ is pale yellow
Main absorption bands of RE ³⁺ ion in aqueous solution in the range 200–1000 nm	—	—	—	210.5, 222.0, 238.0, 252.0	444.5, 469.0, 482.2, 588.5	354.0, 521.8, 574.5, 739.5, 742.0, 797.5, 803.0, 868.0	548.5, 568.0, 702.5, 735.5	362.5, 374.5, 402.0	375.5, 394.1

(Continued)

TABLE 1.2 (CONTINUED)
Properties of Rare-Earth Elements

Properties	Scandium	Yttrium	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium
Color of oxide, RE ₂ O ₃		White	White	Off white (CeO ₂)	Yellow-green; black (Pr ₆ O ₉); pale blue (Pr ₂ O ₃)	Pale blue	Pink	Cream	White
Number of isotopes: natural (artificial) Thermal neutron absorption cross section: for naturally occurring mixture of isotopes, single isotopes (mass number of isotope), barns/atom		1 (14)	2 (19)	4 (15)	1 (14)	7 (7)	(15–18)	7 (11)	2 (16)
		1.31	8.9	0.73	11.6	50	–	5600; 66,000 (149)	4300; 9000 (151); 5000 (152); 420 (153); 1500 (154); 13,000 (155)
									5.67
Ionization potential, eV/g-atom		6.6	5.61	5.65	5.76	6.31	–	5.6	
Electronegativity		1.177	1.117	(+3) 1.123; (+4) 1.43	1.130	1.134	1.139	1.145	(+2) 0.98; (+3) 1.152 (Continued)

TABLE 1.2 (CONTINUED)
Properties of Rare-Earth Elements

Properties	Scandium	Yttrium	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium
Thermal, Electrical, and Magnetic Properties									
Melting point, °C	1541	1522	918	798	931	1021	1042	1074	822
Boiling point, °C	2831	3338	3457	3426	3512	3068	—	1791	1597
Heat of fusion, kJ/mol	14.1	11.4	6.20	5.46	6.89	7.14	(7.7)	8.62	9.21
Heat of sublimation at 25°C, kJ/mol	377.8	424.7	431.0	422.6	355.6	327.6	(348)	206.7	175.3
Allotropic transformation temperature, °C	cph to bcc, 1337	cph to bcc, 1478	deph to fcc, 310; fcc to bcc, 865	fcc to deph, -148; deph to fcc, 139; fcc to bcc, 726	deph to bcc, 795	deph to bcc, 863	deph-bcc, 890	rhomb to cph, 734; cph to bcc, 922	—
Heat of transformation, kJ/mol	cph to bcc, 4.00	cph to bcc, 4.99	deph to fcc, 0.36; fcc to bcc, 3.12	fcc to deph and deph to fcc, 0.05; fcc to bcc, 2.99	deph to bcc, 3.17	deph to bcc, 3.03	deph to bcc, (3.0)	rhomb to cph, 0.2; cph to bcc, 3.11	—
Heat capacity at 298 K, C _p , J/mol·K	25.5	26.5	27.1	26.9	27.4	27.4	(27.3)	29.5	27.7
Standard entropy, S° ₂₉₈ , J/mol·K	34.6	44.4	56.9	72.0	73.9	71.1	(71.6)	69.5	77.8
Coefficient of thermal expansion, per °C	10.2 × 10 ⁻⁶	10.6 × 10 ⁻⁶	12.1 × 10 ⁻⁶	6.3 × 10 ⁻⁶	6.7 × 10 ⁻⁶	9.6 × 10 ⁻⁶	(11 × 10 ⁻⁶)	12.7 × 10 ⁻⁶	35.0 × 10 ⁻⁶
Thermal conductivity, W/(cm·K)	0.158	0.172	0.134	0.113	0.125	0.165	(0.15)	0.133	(0.139)

(Continued)

TABLE 1.2 (CONTINUED)
Properties of Rare-Earth Elements

Properties	Scandium	Yttrium	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium
Magnetic moment (theoretical for 3+ ion), Bohr magnetons		0	0	2.5	3.6	3.6	—	1.5	3.5
Magnetic susceptibility, emu/g·atom		191×10^{-6}	101×10^{-6}	2430×10^{-6}	5320×10^{-6}	5650×10^{-6}	—	1275×10^{-6}	$33,100 \times 10^{-6}$
Curie temperature, °C		None	None	None	None	None	—	None	None
Néel temperature, °C		None	None	−260.6	None	−253	—	−258	−165
Superconducting transition temperature, K	0.050 (at 18.6 GPa)	1.3 (at 11 GPa)	5.10	0.022 (at 2.2 GPa)					
Electrical resistivity, μΩ·cm	56.2	59.6	61.5	74.4	70.0	64.3	(75)	94.0	90.0
Hall coefficient, V·cm/A·Oe	-0.13×10^{-12}	—	-0.35×10^{-12}	$+1.81 \times 10^{-12}$	+0.709	$+0.971 \times 10^{-12}$	—	-0.21×10^{-12}	$+24.4 \times 10^{-12}$
Work function, eV	3.5	3.23	3.3	2.84	2.7	3.3	3.07	3.3	2.54
Density of liquid rare-earth metal, g/cm ³	2.80	4.24	5.96	6.68	6.59	6.72	(6.9)	7.16	4.87
Heat capacity of liquid rare-earth metal, C _p J/mol·K	(44.2)	43.1	34.3	37.7	43.0	48.8	(50)	(50.2)	38.1

(Continued)

TABLE 1.2 (CONTINUED)
Properties of Rare-Earth Elements

Properties	Scandium	Yttrium	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium
				Mechanical Properties					
Yield strength, 0.2% offset, MPa	173	42	126	28	73	71	—	68	—
Ultimate tensile strength, MPa	255	129	130	117	147	164	—	156	—
Uniform elongation, %	5.0	34.0	7.9	22	15.4	25.0	—	17.0	—
Reduction in area, %	8.0	—	—	30	67.0	72.0	—	29.5	—
Young's modulus, GPa	74.4	63.5	36.6	33.6	37.3	41.4	(46)	49.7	18.2
Shear modulus, GPa	29.1	25.6	14.3	13.5	14.8	16.3	(18)	19.5	7.9
Bulk modulus, GPa	56.6	41.2	27.9	21.5	28.8	31.8	33	37.8	8.3
Poisson's ratio	0.279	0.243	0.280	0.24	0.281	0.281	(0.28)	0.274	0.152
Recrystallization temperature, °C	550	550	300	325	400	400	(400)	440	300
Vicker's hardness, 10 kg load, kg/mm ²	85	38	37	24	37	35	—	45	17
Compressibility at 25°C, cm ² /kg	2.26 × 10 ⁻⁶	2.68 × 10 ⁻⁶	4.04 × 10 ⁻⁶	4.1 × 10 ⁻⁶	3.21 × 10 ⁻⁶	3.00 × 10 ⁻⁶	2.8 × 10 ⁻⁶	3.34 × 10 ⁻⁶	8.29 × 10 ⁻⁶
Properties	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium	
Atomic number	64	65	66	67	68	69	70	71	
Atomic weight	157.25	158.92534	162.50	164.93032	167.26	168.93421	173.04	174.967	

(Continued)

TABLE 1.2 (CONTINUED)
Properties of Rare-Earth Elements

Properties	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
Crystal structure	cph < 1235 bcc > 1235	cph < 1289 bcc > 1289	cph < 1381 bcc > 1381	cph	cph	cph	cph < 795 bcc > 795	cph
Atomic volume, cm ³ /mol at 24°C	19.903	19.310	19.004	18.752	18.449	18.124	24.841	17.779
Density, g/cm ³ at 24°C	7.901	8.230	8.551	8.795	9.066	9.321	6.966	9.841
Conduction electrons	3	3	3	3	3	3	2	3
Valence in aqueous solution	3	3	3	3	3	3, 2	3, 2	3
Color in aqueous solution, RE ³⁺	Colorless	Very pale pink	Pale yellow-green	Yellow	Pink	Greenish tint	Colorless; Yb ²⁺ is yellow	Colorless
Main absorption bands of RE ³⁺ ion in aqueous solution in the range 200–1000 nm	272.9, 273.3, 275.4, 275.6	284.4, 350.3, 367.7, 487.2	350.4, 365.0, 910.0	287.0, 361.1, 416.1, 450.8, 537.0, 641.0	364.2, 379.2, 487.0, 522.8, 652.5	360.0, 682.5, 780.0	975.0	None
Color of oxide, RE ₂ O ₃	White	Brown (Tb ₄ O ₇)	Yellowish white	Yellowish white	Pink	White, greenish tint	White	White
Number of isotopes: natural (artificial)	7 (11)	1 (17)	7 (12)	1 (18)	6 (12)	1 (17)	7 (10)	2 (14)
Thermal neutron absorption cross section: for naturally occurring mixture of isotopes, single isotopes (mass number of isotope), barns/atom	46,000; 70,000 (155); 180,000 (157)	46	950; 130 (161); 680 (161); 240 (162); 220 (163); 2780 (164)	64	160	125	37	80

(Continued)

TABLE 1.2 (CONTINUED)
Properties of Rare-Earth Elements

Properties	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
Ionization potential, eV/g-atom	6.16	6.74	6.82				6.25	5.0
Electronegativity	1.160	1.168	1.176	1.184	1.192	1.200	(+2) 1.02; (+3) 1.208	1.216
Thermal, Electrical, and Magnetic Properties								
Melting point, °C	1313	1356	1412	1474	1529	1545	819	1663
Boiling point, °C	3266	3223	2562	2695	2863	1947	1194	3395
Heat of fusion, kJ/mol	10.0	10.79	11.06	(17.0)	19.9	16.8	7.66	(22)
Heat of sublimation at 25°C, kJ/mol	397.5	388.7	290.4	300.8	317.1	232.2	152.1	427.6
Allotropic transformation temperature, °C	cph to bcc, 1235	cph to bcc, 1289	cph to bcc, 1381				fcc to bcc, 795	
Heat of transformation, kJ/mol	cph to bcc, 3.91	cph to bcc, 5.02	cph to bcc, 4.16				fcc to bcc, 1.75	
Heat capacity at 298 K, C _p , J/mol·K	37.1	28.9	27.7	27.2	28.1	27.0	26.7	26.8
Standard entropy, S°298, J/mol·K	67.9	73.3	75.6	75.0	73.2	74.0	59.8	51.0
Coefficient of thermal expansion, per °C	9.4 × 10 ⁻⁶ (at 100°C)	10.3 × 10 ⁻⁶	9.9 × 10 ⁻⁶	11.2 × 10 ⁻⁶	12.2 × 10 ⁻⁶	13.3 × 10 ⁻⁶	26.3 × 10 ⁻⁶	9.9 × 10 ⁻⁶
Thermal conductivity, W/(cm·K)	0.105	0.111	0.107	0.162	0.145	0.169	0.385	0.164
Magnetic moment (theoretical for 3+ ion), Bohr magnetons	7.95	9.7	10.6	10.6	9.6	7.6	4.5	0

(Continued)

TABLE 1.2 (CONTINUED)
Properties of Rare-Earth Elements

Properties	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
Magnetic susceptibility, emu/g-atom	356,000 × 10 ⁻⁶	193,000 × 10 ⁻⁶	99,800 × 10 ⁻⁶	70,200 × 10 ⁻⁶	44,100 × 10 ⁻⁶	26,100 × 10 ⁻⁶	71 × 10 ⁻⁶	17.9 × 10 ⁻⁶
Curie temperature, °C	17	-53	-185	-254	-253	(-241)	None	None
Néel temperature, °C	none	-43	-97	-143	-188	-216	None	None
Superconducting transition temperature, K	—	—	—	—	—	—	—	0.022 (at 4.5 GPa)
Electrical resistivity, μΩ-cm	131.0	115.0	92.6	81.4	86.0	67.6	25.0	58.2
Hall coefficient, V·cm/A·Oe	-4.48 × 10 ⁻¹² (at 77 K)	—	—	—	—	-1.8 × 10 ⁻¹²	3.77 × 10 ⁻¹²	-0.535 × 10 ⁻¹²
Work function, eV	(3.07)	(3.09)	(3.09)	(3.09)	(3.12)	(3.12)	(2.59)	(3.14)
Density of liquid rare-earth metal, g/cm ³	7.4	7.65	8.2	8.34	8.6	(9.0)	6.21	9.3
Heat capacity of liquid rare-earth metal, C _p , J/mol·K	37.2	46.5	49.9	43.9	38.7	41.4	36.8	(47.9)
Mechanical Properties								
Yield strength, 0.2% offset, MPa	15	—	43	—	60	—	7	—
Ultimate tensile strength, MPa	118	—	139	—	136	—	58	—
Reduction in area, %	56.0	—	30.0	—	11.9	—	92.0	—
Young's modulus, GPa	54.8	55.7	61.4	64.8	69.9	74.0	23.9	68.6
Shear modulus, GPa	21.8	22.1	24.7	26.3	28.3	30.5	9.9	27.2
Bulk modulus, GPa	37.9	38.7	40.5	40.2	4.4	44.5	30.5	47.6
Poisson's ratio	0.259	0.261	0.247	0.231	0.237	0.213	0.207	0.261

(Continued)

TABLE 1.2 (CONTINUED)
Properties of Rare-Earth Elements

Properties	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
Recrystallization temperature, °C	500	500	550	520	520	600	300	600
Vicker's hardness, 10 kg load, kg/mm ²	57	46	42	42	44	48	21	77
Compressibility at 25°C (cm ² /kg)	2.56 × 10 ⁻⁶	2.45 × 10 ⁻⁶	2.55 × 10 ⁻⁶	2.47 × 10 ⁻⁶	2.39 × 10 ⁻⁶	2.47 × 10 ⁻⁶	7.39 × 10 ⁻⁶	2.38 × 10 ⁻⁶
Properties	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
Atom	5d6s ²	4f ¹ 5d ¹ 6s ²	Electronic Configuration 4f ³ 6s ² 4f ³ 4f ² 4f					
M ²⁺	5d	4f ²						
M ³⁺	[Xe]	4f						
M ⁴⁺		[Xe]						
Radii, M ³⁺	1.061	1.034	1.013	0.995	—	—	—	0.938
Vapor pressure at m.p., Pa	34.7 × 10 ⁻⁹	0.113 × 10 ⁻⁹	Equilibrium Vapor Pressure 14.67 × 10 ⁻⁶ 4.53 × 10 ⁻³					
Temperature (°C) for vapor pressure 10 ⁻⁸ atm (0.001 Pa)	1301	1290	1083	955	—	508	399	1167
10 ⁻⁶ atm (0.101 Pa)	1566	1554	1333	1175	—	642	515	1408
10 ⁻⁴ atm (10.1 Pa)	1938	1926	1701	1500	—	835	685	1760
10 ⁻² atm (1013 Pa)	2506	2487	2305	2029	—	1150	964	2306
1 atm (101,300 Pa)	3464	3443	3520	3074	—	1794	1529	3273

(Continued)

M^{3+} ions because they then attain the stable $4f^{14}$ and $4f^7$ configurations, respectively. The most stable M^{2+} and M^{4+} ions are formed by those rare earths that can thereby attain f^0 , f^7 , or f^{14} configuration. Thus, Ce^{4+} and Tb^{4+} attain the f^0 and f^7 configurations, respectively, and Eu^{2+} and Yb^{2+} attain the f^7 and f^{14} configurations, respectively. In other words, the special stability of the f^0 , f^7 , and f^{14} configurations is an important factor in determining the existence of oxidation states other than +3 in the rare earths. However, there could be other thermodynamic and kinetic factors that are of equal or greater importance in determining the stability of the oxidation states.

1.3.2 LANTHANIDE CONTRACTION

The term *lanthanide contraction* is used to denote the significant and steady decrease in the size of atoms and ions with the increase in atomic number as the lanthanide series is traversed from lanthanum to lutetium. Thus, as given in Table 1.2 and Figure 1.2, lanthanum has the largest and lutetium the smallest radius. The cause of the contraction is stated to be the imperfect shielding of one electron by another in the same subshell. As one proceeds from lanthanum to lutetium, both the nuclear charge and the number of $4f$ electrons increase by one with each succeeding element. Owing to the shape of the f orbitals, the shielding of one $4f$ electron by another is very imperfect. The atomic nucleus is poorly shielded by the highly directional $4f$ electrons, and as a result, at each increase of the atomic number, the effective nuclear charge experienced by the $4f$ electron increases, resulting in a reduction in the size or contraction of the entire $4f$ shell. With the successive increase in atomic number, such

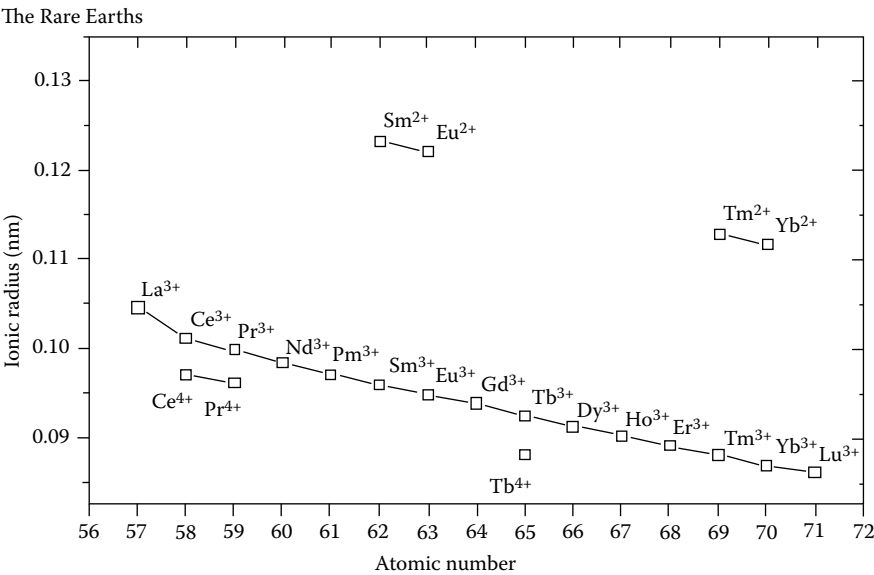


FIGURE 1.2 Lanthanide contraction.

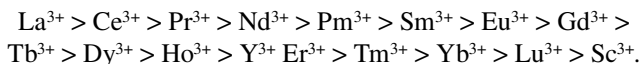
contractions accumulate and result in the steady decrease in size. This is the famous lanthanide contraction.

Lanthanide contraction is the root cause of many of the features of the rare earths' chemistry. The chemistry of lanthanides is predominantly ionic and is determined primarily by the size of the M^{3+} ion. Even though the lanthanum atom and its tripositive ion are considerably larger in size than the corresponding yttrium species, the magnitude of lanthanide contraction is so much that the radii of the lanthanide species decrease to those of the yttrium species in the general holmium–erbium region. The similarity in the outermost electronic arrangement and the similarity in size due to lanthanide contraction explain the occurrence of yttrium in association with the heavier lanthanides. For essentially the same reason, it will be seen later that (1) yttrium compounds always concentrate with those of the heavier lanthanide elements in almost all fractionation procedures for the rare earths' separation, (2) considerable difficulty is experienced in separating yttrium from the heavier lanthanides, and (3) yttrium exhibits general similarities in solubility, crystal structure, and overall chemical properties with the heavier lanthanide metals. These factors, combined with the greater natural abundance of yttrium compared to the heavier rare earths, led to these rare earths being popularly called the *yttrium earths*. The chemistry of heavier rare earths is essentially the chemistry of yttrium.

The lanthanide contraction was sufficient for decreasing the atomic and ionic sizes of the heavier rare earths to those of yttrium but not to those of scandium. The atomic and trivalent ionic radii of scandium are far too small. Thus, scandium does not occur in rare-earth minerals, and its chemistry is significantly different from that of the other rare-earth elements.

1.3.3 BASICITY

One of the important properties of rare-earth elements, related to their ionic size, which is in turn related to lanthanide contraction, is basicity. Basicity determines, in one way or another, certain important chemical features of rare earths relevant to their extractive metallurgy. Basicity determines the extent to which cations hydrolyze in aqueous solution, the relative solubilities of salts of all types, the ease with which salts containing oxyanions decompose when heated, and the stabilities of complex ions (Moeller 1961). A base tends to lose anions or electrons. Thus, those cations with the least attraction for anions or electrons are considered to be the most basic, and those with the strongest attraction, to be the least basic. Considering size relationships alone, the rare-earth ions are arranged as follows in order of decreasing basicity:



Cerium(IV) is less basic than any of the tripositive species, and all of the dipositive species are more basic than the tripositive species (Moeller and Kremers 1945).

The variation in basicity is the basis of most of the fractionation procedures for separating the rare-earth elements from one another (Moeller 1961). In the so-called

classical separation procedures, exploiting the differences in basicity, a large variety of fractional crystallization and fractional precipitation methods had been used. Later, the techniques of ion exchange and solvent extraction, which again ultimately operate by exploiting basicity differences, have been used. The separations involving selective oxidation and reduction are also related to basicity because final removal from the contaminating tripositive species is usually effected by exploiting basicity differences between the different oxidation states of the element. Moeller (1961) emphasized that were it not for size-induced alterations in basicity, the separation of the rare-earth-metal species would be a nearly unsolvable problem.

A note of caution appears to be in order here. To readily achieve what has been implied in the previous paragraph, basicity differences should be large, the larger the better. Even though the size differences between the end members of the series or between two states of oxidation are substantial, the differences between adjacent members of the series in a given state of oxidation are, at best, very small. Therefore, generally, separations of adjacent members of rare earths remain most difficult. However, there are exceptions, like La^{3+} – Ce^{3+} .

1.4 PROPERTIES

In the elemental form, the rare earths are lustrous, iron gray to silvery metals. They are typically soft, malleable, and ductile and usually reactive. Their reactivity is especially pronounced at elevated temperature or when finely divided.

The physical properties of the rare-earth elements are listed in Table 1.2 (Cannon 1974; Gschneidner and Daane 1988; Gschneidner 1990; Gschneidner et al. 1995; McGill 1997).

1.4.1 MELTING POINT

The melting point increases in a regular manner across the series from lanthanum to lutetium with the exception of cerium, europium, and ytterbium. The melting point of lutetium is almost twice that of lanthanum. While considering the increase in the melting point by as much as 750°C , as the rare-earth series is traversed from lanthanum to lutetium, as unusual for a group of nearly identical elements, Gschneidner and Daane (1988) attribute the change in the melting point to the extent of hybridization of the $4f$ and $5d6s$ orbitals. The hybridization is the largest for cerium (the lowest-melting rare-earth metal) and decreases along the series from light lanthanides to heavy lanthanides. A lower melting point is associated with a greater amount of hybridization.

Various values have been reported for the melting points of the rare-earth metals, and this variety is traceable to the purity of the metal and the method used for the determination of the melting point. The temperature at which the rare-earth metal melts depends on its purity. If appreciable quantities of oxygen, carbon, and nitrogen are present in the sample, the measured melting points are likely to be high (Spedding et al. 1968). In small quantities, these impurities can lead to lower readings of the melting point (Gschneidner and Daane 1988). For example, early reports on the melting point of lanthanum put it at 806°C , but the currently accepted

value is 918°C. The determination of the La–C phase diagram by Spedding et al. (1959) revealed that the La–C eutectic melts at 806°C. Earlier, samples of lanthanum metal were prepared by fused-salt electrolysis using graphite electrodes, and melting point determinations using these samples, usually contaminated with carbon, led to the eutectic being reported as the pure metal's melting point. The availability of relatively large amounts of metallothermically prepared pure rare-earth metals in the 1950s led to more accurate determination of their melting points. Melting point determined by thermal analysis using a refractory metal crucible also needs to be checked for the possibility of the eutectic being reported as the melting point. In tantalum, however, the eutectic point and the actual melting point are very close to each other, differing by less than 1°C, in low-melting rare earths, but the difference may be appreciable in high-melting rare earths (Garg et al. 1996). The difference between the eutectic temperature and the actual melting point is much smaller in the corresponding rare earth–tungsten systems (Krishnamurthy et al. 2000).

The melting point of the rare-earth metal is an important parameter in the choice of the reduction process for metal production, both by metallothermic and electrolytic routes. Relatively inexpensive chloride reduction processes can be used for producing certain low-melting rare-earth metals (La, Ce, misch metal), whereas more expensive fluoride reduction methods are needed for the high-melting rare-earth metals (Gd, Y).

1.4.2 BOILING POINT

The vapor pressures of all the rare-earth metals were systematically determined at Ames Laboratory in the 1950s using the Knudsen effusion technique for all the rare-earth metals except promethium. Their data along with the values for promethium are included in Table 1.2.

The boiling points of rare-earth metals do not exhibit a trend, even to the extent, the melting points displayed, across the series. Lanthanum metal, which is among the four lowest-melting-point rare earths, has the highest boiling point. In other words, it has the lowest vapor pressure at its melting point for any rare-earth metal. The most volatile rare-earth metal is ytterbium. At 1000°C, for example, the vapor pressure of lanthanum is one-billionth of the vapor pressure of ytterbium (Gschneidner and Daane 1988). The heat-of-vaporization data for the rare earths are also listed in Table 1.2. Habermann and Daane (1961) noted certain correlations among the vapor pressure (boiling point), heat of vaporization, and electronic structure of the rare-earth metals. For example, the divalent europium and ytterbium in the metallic state have no *d* electrons, resulting in weaker bonding. Consequently, the vapor pressure is higher, and the heat of vaporization is lower. Later, Gschneidner and Daane (1988) considered the electronic states of both the condensed phase and the final gaseous atom in correlating the electronic structure to boiling point and heat of vaporization.

Like the melting point, the boiling point of a rare-earth metal also strongly influences the method used for its preparation and purification. For example, the most volatile metals—europium, samarium, and ytterbium—are prepared by the reduction–distillation process, which is very similar to the Pidgeon process used for

magnesium (Pidgeon and King 1948). In these and other metals, the high vapor pressures are also exploited for the purification of metal by sublimation or distillation (Beaudry and Gschneidner 1978). On the other hand, the relatively high volatility of many of the rare-earth metals has been a major limitation in the application of ultrapurification techniques like solid-state electrotransport.

1.4.3 ALLOTROPES

The crystal structures and lattice parameters of all the rare-earth metals, except samarium, promethium, and holmium, were determined quite early by Klemm and Bommer (1937). Their work confirmed the existence of the lanthanide contraction; discovered the multivalency in cerium, europium, and ytterbium; and confirmed that the rare earths crystallize in at least three different structures: fcc, bcc, and hcp. Final and finer details of room-temperature crystal structures of rare-earth metals were established at Ames Laboratory by various researchers between 1958 and 1971. The details of crystal structures, lattice parameters, and allotropic transformation temperatures of rare earths are summarized in Table 1.2.

Most of the rare-earth metals crystallize in the close-packed hexagonal structure. However, the stacking sequence along the *c*-axis is not identical for all. Lanthanum, cerium, praseodymium, and neodymium crystallize with one stacking sequence; gadolinium to lutetium crystallize in another; and samarium has yet another arrangement. Most of the rare-earth metals undergo allotropic transformation, and the high-temperature phase just below the melting point is invariably bcc. Europium, which is bcc even at room temperature, undergoes no transformation. Holmium, erbium, thulium, and lutetium also are monomorphic (cph) and do not undergo an allotropic transformation to the bcc phase before melting at atmospheric pressure. However, by application of pressure (~1 GPa), the bcc phase can be transformed in holmium and erbium. As regards the allotropic transformation temperatures, there is apparently no systematic trend across the lanthanide series (Gschneidner and Daane 1988).

The allotropic transformation is important in rare-earth-metal ultrapurification. The electrotransport mobilities of interstitial impurities in rare-earth metals depend on the crystal structure of the metal. Mobility is higher in the bcc phase. Thus, when no other complication crops up, electrotransport purification is best carried out in the bcc phase.

The light rare earths form solid solutions with each other, and so do the heavy rare earths. The solid solution is not perfect, and the liquidus and solidus lines are curved. When a light rare earth is alloyed with a heavy rare earth, two phases are likely to form.

1.4.4 RESISTIVITY

The rare-earth metals are poor electrical conductors. Among the rare earths, room temperature resistivities are highest in the middle of the series. They also show anisotropy. Resistivity measured along the *c*-axis of a rare-earth-metal single crystal differs from that measured along the *a*- or *b*-axis in the basal plane. Rare earths are self-resistance heated during their purification by solid-state electrotransport.

The resistivity of the metal at 4 K is sensitive to the presence of impurities, particularly oxygen, nitrogen, and hydrogen, to the extent that it can be used for denoting the metal purity. A well-known method for estimating the total purity of a metal is to measure the ratio of its resistivities at 298 K and at 4 K, or even at 1 K. The impurities will be very low if the resistivity ratio obtained is very high. For certain rare earths, however, in spite of good purity, the resistivity ratio obtained may not be very high.

Among the rare earths, only lanthanum is superconducting at atmospheric pressure (Gschneidner and Daane 1988), and elemental lanthanum (fcc phase) is one of the better elemental superconductors [$T_c = 6.1$ K, $H_c(0) = 1600$ Oe], like lead ($T_c = 7.2$ K) and niobium ($T_c = 9.2$ K). At a high pressure of 20 GPa, lanthanum has the highest known elemental superconducting transition temperatures (13 K). Certain lanthanum-based ceramic compositions are important superconducting materials.

1.4.5 MAGNETIC PROPERTIES

The $4f$ electrons determine the magnetic behavior of the rare-earth metals. In the completed $4f$ subshell, the magnetic effects of different electrons cancel each other out, but in the incomplete $4f$ subshell, they do not. All rare-earth metals, except scandium, yttrium, lanthanum, ytterbium, and lutetium, are strongly paramagnetic. On cooling, many of them become antiferromagnetic, and on cooling further, a number of these elements become ferromagnetic. If a magnetic field of sufficient strength is applied, all paramagnetic rare earths become ferromagnetic at low temperatures. The rare-earth metals display strong magnetic anisotropy; their magnetic behavior depends on the crystal axis.

The existence of ferromagnetism at room temperature in gadolinium was reported and confirmed by Klemm and Bommer (1937). Many of the detailed studies on the magnetic behavior of the rare-earth elements were carried out by the Ames group in the 1950s. Elucidation of the magnetic behavior of the rare-earth metals, as has been the case with their many other properties, was greatly dependent on the availability of the rare-earth metals at high levels of purity and in special forms such as large single crystals (Gschneidner and Daane 1988).

1.4.6 SPECTRAL PROPERTIES

The trivalent rare-earth ions, except Ce^{3+} and Yb^{3+} , exhibit very sharp absorption bands in the visible and ultraviolet (UV) regions. These bands are caused by f - f transitions, and the sharpness comes because the electrons in the $4f$ inner shell of the rare earths are shielded from the chemical environment by the $5s^2 5p^6$ octet. Most of the rare-earth salts display colors that are characteristic of the tripositive ions. The striking colors persist in aqueous and nonaqueous solutions and are unaffected by alterations of anions present or the addition of complexing agents (Moeller 1971). The absorption bands and colors are listed in Table 1.2.

In the rare earths with electronic configurations of $4f^1$ and $4f^{13}$, no f - f transition is possible. Thus, Ce^{3+} and Yb^{3+} do not absorb in the visible region. They do, however,

absorb in the UV region due to transitions of the type $4f^n-4f^{n-1}5d$. The divalent ions of europium, samarium, and ytterbium display colors in aqueous solutions: Eu^{2+} is pale yellow, Sm^{2+} is deep red, and Yb^{2+} is yellow.

1.4.7 MECHANICAL PROPERTIES

Values for the elastic and mechanical properties of rare-earth metals reported in the literature vary widely. This is because of the variation in the impurity levels of the metals. Generally, the elastic property values increase with an increase in purity (Gschneidner and Daane 1988). The chosen values are listed in Table 1.2 (Gschneidner 1990). In the series, there is an increase in the elastic moduli with an increase in atomic number until a maximum is reached at thulium. Cerium, europium, and ytterbium have anomalously low values. The elastic constants of rare earths are similar in value to those of aluminum, zinc, cadmium, and lead.

The hardness and strength values of the rare earths (Gschneidner and Daane 1988; Gschneidner 1990) follow the same periodic trend displayed by the elastic constants. Cerium, europium, and ytterbium have anomalously low values. Mechanical properties improve from the light rare earths to the heavy rare earths. In the lower range, the strengths of rare-earth metals are similar to that of aluminum, and in the higher range, the values correspond to levels between aluminum and titanium.

1.5 REACTIVITY

1.5.1 AIR/OXYGEN

At room temperature, all the rare-earth metals are not affected by air the same way. Some corrode very rapidly, while some remain bright and shiny for years. A solid block of europium tarnishes immediately on exposure to air at room temperature, particularly when the air is moist. If left in that condition, it will be converted to an oxide of europium in a few days or weeks. Massive blocks of lanthanum, under similar conditions, will undergo surface corrosion in a few days and will develop a thick crust of oxide in a few months. Neodymium behaves in the same way as lanthanum; however, most of the heavy rare-earth metals will remain bright for a long time.

An increase in temperature and humidity accelerates oxidation of rare-earth metals (Gschneidner and Daane 1988). The rate at which lanthanum oxidizes increases by more than a factor of 10 when the relative humidity is increased from 1% to 75%. The oxidation of lanthanum at 1% humidity, which is 0.8 mg/cm^2 day at 35°C , increases to 5.1 mg/cm^2 day at 95°C , rising further to 32 mg/cm^2 day at 400°C and to 130 mg/cm^2 day at 600°C (Love and Kleber 1960). The value at 75% relative humidity is 210 mg/cm^2 day at 95°C . Under the latter conditions, praseodymium oxidizes at the rate of 55 mg/cm^2 day, neodymium at 20 mg/cm^2 day, and samarium at 1 mg/cm^2 day. The corresponding values for gadolinium through lutetium, scandium, and yttrium are $0-0.35 \text{ mg/cm}^2$ day. The oxide products formed by the oxidation of the light rare earths, lanthanum through neodymium, are the hexagonal (A)-form RE_2O_3 phase. Samarium through gadolinium form the monoclinic (β)-form RE_2O_3 , and the remaining rare earths form the cubic (C)-form RE_2O_3 phase. The A-form oxides

react readily with water vapor in the air to form an oxyhydroxide, and this spalls, exposing the fresh metal surface, which undergoes oxidation. The C-type-structure oxides form a tight coherent stoichiometric gray-black coating, preventing further oxidation. It will be seen later that neodymium being prone to oxidation is a major technological issue in the production and use of NdFeB magnets.

The rate of oxidation is increased considerably if the metal contains one or more impurities such as fluorine, calcium, magnesium, carbon, iron, and any of the many *p*-group elements such as zinc, gallium, and germanium, and their congeners. Pure metals are attacked by oxygen and moisture slowly at first; however, once oxidation starts, the oxide apparently catalyzes the reaction, and oxidation is fast.

1.5.2 REFRACTORIES

The reactivity of rare-earth metals toward oxygen is due to the large negative free energy of formation of the oxide, and the free energy of formation of rare-earth oxide is among the most negative of all the elements in the periodic table. In other words, the rare-earth oxides are among the most stable of the oxides of all elements in the periodic table. At room temperature, only calcia is more stable than the rare-earth oxides. As a consequence, the rare-earth metals will attack and reduce most of the refractory crucibles, including zirconia, alumina, and magnesia and such refractory linings (Kremers 1961). The attack on refractories is particularly relevant when containment of the liquid rare-earth metal is considered. Rare-earth metals form solid solutions with oxygen. These solutions have greater stability (Alcock 1976), and this leads to the rare-earth metal picking up and dissolving oxygen from oxides of comparable (e.g., MgO) or greater (e.g., CaO) stability.

The Ellingham diagram showing the stabilities of certain well-known oxide refractories, rare-earth oxides, and rare-earth metal–oxygen solid solutions is given in Figure 1.3 (Okabe et al. 1998) and Figure 1.4 (Hirota et al. 1999). That the metal–oxygen solid solutions are far more stable than the lowest oxides of metal concerned at all temperatures is clearly revealed. Besides, the more dilute the solid solution is, the greater is its stability. The equivalent partial pressure of oxygen corresponding to various regions of the Ellingham diagram is also shown. Thermodynamically, all known oxide refractories will be attacked by the rare-earth metals, when heated together. It is also shown that the solution of oxygen in yttrium metal is the most stable metal–oxygen system among all the oxides and oxygen solutions.

1.5.3 NITROGEN

Rare-earth metals show a strong affinity for nitrogen. The mononitrides of rare earths are comparable in stability to those formed by metals such as titanium or zirconium (Pankratz et al. 1984). They have high melting points and very low decomposition pressures. The metals also form solid solutions with nitrogen. For example, cerium dissolves up to 0.3 wt.% nitrogen at 750°C. The equilibrium nitrogen pressures over these solutions will be still lower. Thus, the rare earths are very good getters of nitrogen from the environment and do not easily degas with respect to nitrogen.

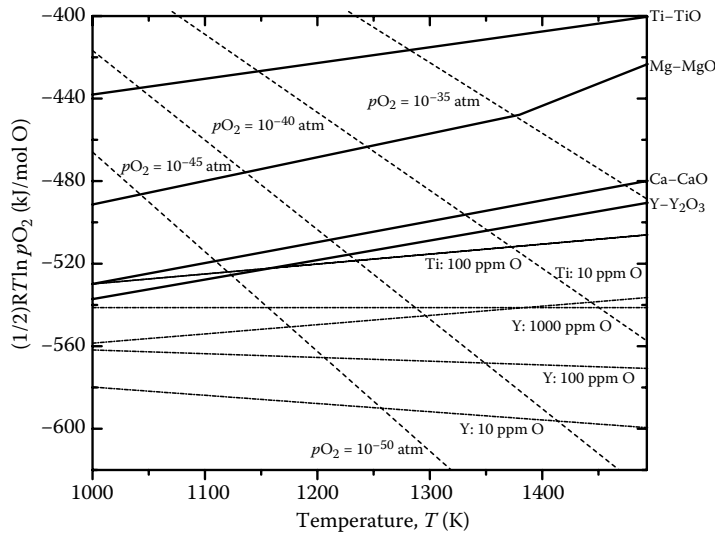


FIGURE 1.3 Ellingham diagram showing the stabilities of certain well-known oxide refractories, yttria, and titanium, yttrium-oxygen solid solutions. (From Okabe, T.H. et al. *J. Alloys. Compounds*, 237: 150–154, 1996.)

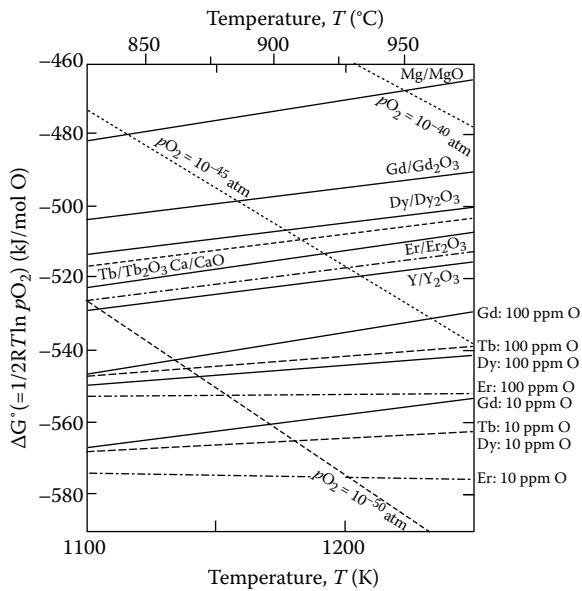


FIGURE 1.4 Ellingham diagram showing the stabilities of selected oxides and the oxygen chemical potential of RE-O (RE = Gd, Tb, Dy, Er) solid solutions containing 10 and 100 mass ppm of oxygen. (From Hirota K. et al., *J. Alloys. Comp.*, 282(1–2): 101–108, 1999.)

The reaction between rare-earth metals and nitrogen is, however, slow. High temperatures are needed to observe any appreciable reaction. Besides, the formation of a nitride layer on the surface greatly retards further nitridation.

1.5.4 HYDROGEN

Rare-earth metals react with hydrogen and easily form hydrides at temperatures of 400–600°C. If hydriding is allowed to continue, when the metal is hydrided up to and beyond REH_2 , the solid material fragments. When the hydrogen content is below REH_2 , the material behaves like a metal and, at certain concentrations of hydrogen, conducts electricity better than even the pure metal. It is possible to load more hydrogen per unit volume in yttrium metal than in liquid hydrogen or water. The decomposition pressure of YH_2 is low even at fairly high temperatures and becomes 1 atm only at 1260°C (Spedding et al. 1968).

Unlike the yttrium hydride, several rare-earth-metal hydrides decompose and degas evolving hydrogen at relatively low temperatures. The brittleness and crumbling tendency of the hydride, combined with the possibility of easy hydrogen removal by degassing, has made hydriding–comminution–dehydriding a method to produce rare-earth-metal powder. It is, however, likely that the effort to drive off the last traces of hydrogen from the powdered hydride, by the use of high temperatures, will result in a partially sintered mass of powder (Gschneidner and Daane 1988).

1.5.5 CARBON

All rare earths are known to form dicarbides RE_2C_2 , and most of them (La–Sm, Gd–Ho, Y) form sesquicarbides, RE_2C_3 . Monocarbides (e.g., ScC, LaC) and subcarbides (e.g., RE_3C_4 , Sm, Gd–Lu) are also known (Goldschmidt 1967). The rare-earth carbides are high melting and form extensive solid solutions with oxygen and nitrogen. The solid solubility of carbon in rare-earth metals is also considerable (Massalski et al. 1990). For example, yttrium dissolves up to 1.3 wt.% C at 1520°C, and lanthanum takes up to 0.3 wt.% C at 775°C. The high stability of the lower carbides of rare earths and also of the carbon–RE solutions makes the attack of molten rare-earth metals on graphite crucibles an important factor leading to the contamination of rare-earth metals with carbon. Besides, these characteristics have rendered carbothermic reduction a useless method for rare-earth-metal preparation.

1.5.6 SILICON

Silicon, like carbon, forms rare-earth silicides and solid solutions. Rare-earth silicides are generally all disilicides represented by the formula RESi_2 , but silicides of other stoichiometries have also been reported (Goldschmidt 1967).

1.5.7 SULFUR, SELENIUM, PHOSPHORUS

The rare earths react exothermically with sulfur, selenium, and phosphorus. On heating a mixture of rare-earth metal with these elements, the reaction sets off and,

if precautions are not taken, could seriously damage the crucible, furnace, vacuum enclosures, etc. The strong exothermicity may afford preparation of sulfides, selenides, and phosphides of rare earths by self-propagating high-temperature synthesis (SHS). On the other hand, at low temperatures, some of the rare earths, particularly heavy rare earths, hardly react with, for example, sulfur.

1.5.8 REFRACTORY METALS

Among the refractory metals, niobium, molybdenum, tantalum, and tungsten are resistant to attack by liquid rare-earth metals. The metals listed above are in order of decreasing solubility in the liquid rare-earth metals at high temperatures, tungsten being the least soluble (Dennison et al. 1966a,b). Approximately 1.5 at.% tantalum dissolves in lutetium at the eutectic temperature, and the corresponding solubility of tantalum in scandium is about 3 at.%. When tungsten is used in place of tantalum, the solubility of tungsten in liquid rare-earth metals is about one-third of the solubility of tantalum. This makes tungsten the most inert container for holding liquid rare-earth metals. However, tungsten embrittles and has poor mechanical properties compared to tantalum. Thus, tantalum is a more useful crucible material for liquid rare earths in spite of its solubility in rare earths. The solubility of tantalum is a function of temperature, and for many rare-earth metals, it decreases from a high value at high temperatures to a very low value at temperatures just above the rare-earth metal's melting point.

Commenting on the interaction of tantalum with liquid rare-earth metals, Gschneidner and Daane (1988) have stated that the use of ceramic crucibles for metal preparation and purification puts an upper limit of 95–98 at.% purity of the rare-earth metals. The use of tantalum has allowed the purity level to rise to 99 at.% and higher.

1.5.9 ACIDS AND BASES

All rare-earth metals readily dissolve in dilute mineral acids, and hydrogen is evolved. In a certain range, the rate of dissolution is proportional to the acid concentration (Gschneidner and Daane 1988). The attack on the metal by concentrated sulfuric acid is somewhat less (Kremers 1953). Rare-earth metals resist attack by hydrofluoric acid because REF_3 forms and coats the metal. This coating prevents further attack by the acid. A mixture of equal parts of concentrated nitric acid and 48% hydrofluoric acid attacks most rare earths only superficially and may be used to clean/pickle the rare-earth metals. This acid mixture may be used to separate tantalum from the rare earths because only tantalum dissolves in the mixtures, whereas the rare earths remain more or less intact (Gschneidner and Daane 1988). Rare-earth metals react with common organic acids but at slower rates than with mineral acids of the same concentration.

Rare-earth metals react, but slowly, with strong bases like sodium hydroxide. With a weak base like ammonium hydroxide, no reaction occurs. The lack of reactivity may be due to the formation of an insoluble rare-earth hydroxide coating on the metal surface.

1.5.10 WATER

The reaction of rare earths with water varies depending on the metal. Generally, light rare-earth metals react with water slowly at room temperature and vigorously at higher temperatures. The heavy rare earths react very slowly. However, even with cold water, europium reacts to form $\text{Eu}(\text{OH})_2 \cdot \text{H}_2\text{O}$, liberating hydrogen (Spedding et al. 1968).

1.6 AQUEOUS SYSTEMS

The standard oxidation potential data listed in Table 1.2 indicate that each of the rare-earth elements is a powerful reducing agent in aqueous acidic solution and forms the tripositive ion readily. The special stability of empty, half-filled, and completely filled $4f$ shells is reflected (Moeller 1967) in that the $4f^0$ cerium(IV) is much less readily reduced to the tripositive state than the $4f^1$ praseodymium(IV). For similar reasons, $4f^7$ europium(II) and $4f^{14}$ ytterbium(II) are weaker reducing agents than samarium(II).

1.6.1 TRIVALENT STATE

The rare earths are characteristically trivalent. In an aqueous solution, the tripositive rare-earth cations have a strong ionic character and form salts with a large variety of anions. The solubilities of such salts vary widely.

Rare-earth hydroxides are obtained as gelatinous precipitates from aqueous solutions by the addition of ammonia or dilute alkalis. Rare-earth hydroxides are definite compounds and are not just hydrous oxides. As mentioned earlier, $\text{La}(\text{OH})_3$ is the most basic of the rare-earth hydroxides, and the basicity decreases across the series with an increase in the atomic number.

Rare-earth salts containing thermally unstable anions such as OH^- , CO_3^{2-} , and $\text{C}_2\text{O}_4^{2-}$, when heated, yield first the basic derivatives and finally the oxides. The hydrated salts, regardless of the nature of the anion, undergo thermal hydrolysis at high temperatures. Anhydrous compounds of rare earths containing thermally stable anions such as O^{2-} , F^- , Cl^- , and Br^- melt without decomposition at relatively high temperatures. These solids are also highly ionic.

The chlorides, bromides, nitrates, bromates, and perchlorate salts of rare earths are all soluble in water. When their aqueous solutions are evaporated, they precipitate as hydrated crystalline salts. For example, the rare-earth chlorides crystallize as hexahydrates. The light rare earths (La to Nd) can form heptahydrates. On heating, the hydrated chlorides lose HCl more readily than H_2O . The product is oxychloride. The bromides and iodides are quite similar to the chlorides. The iodides as well as the iodates and acetates are somewhat less soluble in water. The sulfates are sparingly soluble, and their solubility decreases with an increase in temperature. The rare-earth oxides, sulfides, fluorides, carbonates, oxalates, and phosphates are insoluble in water. Among the halides, only the fluorides are insoluble. The addition of hydrofluoric acid or fluoride ions to RE^{3+} solutions even in 3M nitric acid results in the precipitation of REF_3 . This is a characteristic test for rare-earth ions. Rare

earths can also be precipitated as oxalates, another insoluble rare-earth compound, from a dilute nitric acid solution. The precipitation is not only quantitative but also specific to rare earths and is used for the determination of rare earths gravimetrically. Oxalate precipitation is also a useful procedure for rare-earth purification. The oxalate is calcined to the oxide.

Double salts of rare earths are common and extensively used. The most important are the double nitrates $2\text{RE}(\text{NO}_3)_3 \cdot 3\text{MgNO}_3 \cdot 24\text{H}_2\text{O}$ and $\text{RE}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, and the double sulfates $\text{RE}_2(\text{SO}_4)_3 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{RE}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. The cerium-group double sulfates are only sparingly soluble in sodium sulfate, whereas those of the yttrium group are appreciably soluble. This characteristic makes it possible to achieve a fairly rapid separation of the entire group of rare earths into two subgroups.

1.6.2 COMPLEXES

The formation of complex species is an important feature of tripositive rare-earth ions. It is improbable, however, that any hybrid *f* orbitals from the ions would take part in covalent bonding, and the large size of the RE^{3+} ions makes it possible for only certain types of complexes to be formed (Moeller 1961). Thus, (1) the number of rare-earth complexes is limited; (2) only species that can attract the RE cations as a result of their own small size, large charge, and chelating abilities will yield complexes; (3) stabilities of such complexes with respect to dissociation will be less than those of the tripositive transition metal ions; and (4) bonding in all complex species will be predominantly ionic. The coordination number is usually 7, 8, 9, or 10, and only in isolated cases, it is 6. Properties that depend directly on the 4*f* electrons are not affected by complexation. The complexes formed by tripositive rare-earth ions include complexes with citric acid, ethylene diamine tetraacetic acid (EDTA), and hydroxy ethylene diamine triacetic acid (HEDTA). The most important of the chelates are the species derived from the various polyamine polycarboxylic acids. Many of these have been isolated and characterized. These complexes are water soluble. However, the stabilities of the species in solution are of great importance because differences in the stabilities of the complexes have been used in conjunction with ion-exchange techniques to effect the separation of rare earths from one another (Powell 1961, 1979). The complex formation is pH dependent, and the stabilities of chelates are related to the ionic radii of the rare-earth ion. The stabilities of complex species invariably increase from La^{3+} to Eu^{3+} or Gd^{3+} , but for cations heavier than gadolinium, the stability may continue to increase, remain nearly constant, or pass through a maximum (Moeller 1967).

1.6.3 TETRAVALENT STATE

Cerium(IV) is the only tetrapositive rare-earth species that is stable in aqueous solution as well as in solid compounds (Moeller 1961). The III and IV valency states of cerium are often designated as cerous and ceric, respectively. Ceric oxide, CeO_2 , hydrous ceric oxide, $\text{CeO}_2 \cdot n\text{H}_2\text{O}$, and ceric fluoride, CeF_4 , are the only binary solid compounds of Ce(IV). Ceric oxide is obtained by heating cerium metal, $\text{Ce}(\text{OH})_3$,

or any of the several Ce(III) oxosalts, such as the oxalate, nitrate, or carbonate in air or oxygen. CeO_2 , white when pure, is quite inert and not attacked by even strong acids or alkalies. It can, however, be dissolved by acids in the presence of reducing agents to form Ce(III) solutions. Hydrrous $\text{CeO}_2 \cdot n\text{H}_2\text{O}$ can be obtained as a yellow gelatinous precipitate, from Ce(IV) solutions on treatment with bases. The hydroxide is precipitated at a pH of 1. Ceric fluoride, CeF_4 , is prepared by reacting anhydrous CeCl_3 or CeF_3 with fluorine at room temperature. Ceric fluoride is inert to cold water and is reduced to CeF_3 by hydrogen at 200–300°C.

Ce(IV) is obtained in solution by treatment of Ce(III) solution with strong oxidizing agents like ozone, peroxodisulfate, or bismuthate in nitric acid. Under alkaline conditions, oxidation of cerium to a +4 state is readily effected by OCl^- , H_2O_2 , and O_2 . In solutions, Ce(IV) can also be obtained by electrolytic oxidation. Cerium(IV) forms phosphates insoluble in 4NHNO_3 and iodates insoluble in 6NHNO_3 as well as insoluble oxalate. Precipitation as phosphate or iodate can be used to separate Ce(IV) from trivalent rare earths. Ce(IV) is extracted more readily than the RE(III) ions into organic solvents like tributyl phosphate. Ce(IV) can be used as an oxidizing agent.

Ceric oxide dissolves, undergoing reduction, in acids such as hydrochloric acid. In an acidic medium, reduction of cerium(IV) is effected by many reductants such as Fe^{2+} , Sn^{2+} , I^- , and H_2O_2 . It dissolves in oxidizing acids such as nitric acid or sulfuric acid without undergoing reduction. The double ammonium nitrite of Ce(IV), the orange-red water-soluble salt $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$, crystallizes readily from a concentrated nitric acid solution. It is both an excellent source of Ce(IV) and a useful analytical oxidizing agent.

Pr(IV) is a powerful oxidizing agent and oxidizes water itself. Therefore, it does not exist in aqueous solution. When Pr(III) salt or oxide is heated in air, Pr_6O_{11} forms. Both Pr(III) and Pr(IV) are present in the oxide.

The chemistry of Tb(IV) is similar to that of Pr(IV). The oxide Tb_4O_7 is obtained on igniting Tb(III) oxosalts in air. Tb_4O_7 contains both Tb(III) and Tb(IV). TbO_2 is obtained by oxidation of Tb_2O_3 with atomic oxygen at 450°C. The colorless compound TbF_4 is obtained by treating TbF_3 with gaseous fluorine at 300–400°C.

1.6.4 DIVALENT STATE

The divalent state of Sm, Eu, and Yb is well established both in solution and in solid compounds. These species are obtained (Moeller 1967) by (1) thermal reduction of anhydrous halides or chalcogenides with metals or hydrogen [e.g., solid oxide, chalcogenides, halides, carbonate, or phosphate of europium(II) may be obtained by reduction of the corresponding Eu(III) compound or from EuCl_2 by metathesis]; (2) electrolytic reduction in aqueous solution or in halide melts [e.g., Eu(II) and Yb(II)]; (3) chemical reduction in solution [Eu(II) using Zn in aqueous solution, Sm(II) using Mg in ethanol]; (4) thermal decomposition of anhydrous triiodides; and (5) controlled oxidation of free metals or their amalgams.

The divalent rare-earth cations are strong reducing agents in acidic aqueous solutions, and their reducing ability decreases in the order $\text{Sm}^{2+} \gg \text{Yb}^{2+} \gg \text{Eu}^{2+}$. Both Sm^{2+} and Yb^{2+} undergo instant oxidation to the trippositive species by the hydronium

ion and also by air. The oxidation of Eu^{2+} is, however, slower, and solutions containing Eu^{2+} can be readily handled. In an acidic solution, all three ions are rapidly oxidized by elemental oxygen. The RE^{2+} ions resemble group II ions, particularly Ba^{2+} . Thus, the hydroxides are soluble, and sulfates are insoluble. Eu^{3+} can be readily separated from the other rare earths by reduction with zinc to the dipositive state followed by the precipitation of the remaining tripositive rare earths as hydroxides by carbonate-free ammonia. The water-insoluble compounds, sulfates, carbonates, or fluorides of the divalent ions are relatively more resistant to oxidation. These ions have little tendency, compared to Ba^{2+} or Sr^{2+} , to form complex compounds.

1.7 APPLICATIONS

The rare earths have an ever-growing variety of applications in the modern technology. The first application of the rare earths and the beginning of the rare-earth industry date back to 1891 and were related to the inventions of the Austrian entrepreneur and scientist Carl Auer von Welsbach. He used the rare earths to solve what was, at that time, a major technical problem—the production of bright light. It was already known that a solid of suitable composition and large surface area, when brought into the hot zone of a gas flame, would glow, giving off the required bright light. The hitch was finding a suitable solid that would be the incandescent mantle. Auer solved the problem. First, he announced in 1866 the discovery of a gas mantle composed of zirconia doped with lanthana. That mantle was too brittle and produced cold blue light. Later, after persistent experimentation, in 1891 Auer came up with a gas mantle composed of 99% thoria and 1% ceria. The light from this mantle was not only white and bright and superior to electric light but it was also cheaper. This situation remained for several decades until about 1935, and an estimated 5 billion gas mantles had been produced and consumed in the world (Greinacher 1981). The Auer mantle was produced by a simple process. A cotton sock was saturated with a salt solution, which, upon ignition, resulted in a mixture of thorium–cerium oxides with a large surface area. Even today, light production from gas mantles remains in use in remote areas where electricity is unavailable or erratic and in some railroad signal devices.

The next important application of the rare earths also came from Auer's inventions. The search for a simple ignition system for his gas mantle lamps led him to discover (in 1903) and develop a pyrophoric alloy called flintstone. Beginning in 1903, the production of flintstone was the first major large-scale use for rare-earth metals. The flintstone, which is composed of 70% misch metal and 30% iron, was used in the lighters for the gas mantle. The name *misch metal* was coined by Auer for the alloy that contained lanthanum, cerium, and didymium in the same proportion in which they occurred in monazite. To produce misch metal, Auer founded a company in Carinthia, Austria in 1907. The company came to be known as Treibacher Chemische Werke and was the first company involved in the commercial production of rare earths. Auer used the fused-salt electrolysis method for the production of misch metal, and in 1908, over 800 kg of misch metal–iron flints entered the market. Following Auer's discovery, production of lighter flints was started by Ronson Metals in the United States in about 1915.

Greinacher (1981) noted that in the 22 years between 1908 and 1930, about 1100–1400 t of flints were produced from approximately 1300–1800 t of rare-earth oxides in the form of rare-earth chlorides. During the same time, about 7500 t of thorium nitrate were used for Auer incandescent mantles. The lighter flints are still very common and account for the consumption of a substantial fraction of the misch metal produced. Pyrophoric alloys, which give tracer shells their distinctive fiery trail, also contain misch metal as a constituent.

The production of intense light by electric arc was developed by Beck in Germany in 1910. These electric arc lamps have been used for a wide range of lighting purposes, including searchlights and cinema projectors. Historically, the third major use of rare earths was the addition of rare-earth fluoride as a wick in arc-light carbons (Greinacher 1981). Even though the electric arc struck and maintained between carbon electrodes emits light, it is low in intensity. The brightness is greatly increased if a cored carbon, consisting of an outer shell of carbon and an inner core made from carbon flour mixed with rare-earth oxides and fluorides, is used. The enhanced brightness and color come about because of the characteristic emission spectra of the core material (Bagchi 1988).

From these beginnings, and over many years, applications of rare earths have developed essentially in industrial and technology areas broadly classified as magnets, catalysts, electronics, glass, ceramics, metal alloys, phosphors, and others. The division of the total world rare-earth consumption among these application areas is summarized in Table 1.3 (Gschneidner 2011a,b). The proportion of rare earths (by volume) that is consumed in each of these categories is also listed for the year 2010. An element-wise listing of the major uses of rare earths is given in Table 1.4.

1.7.1 METALLURGY

Rare earths have major applications as metallurgical alloys. The oldest of these alloys is misch metal, which is, as mentioned earlier, an alloy consisting only of rare-earth metals, with the individual rare-earth elements present in the same proportion in which they naturally occur in bastnasite or monazite. Misch metal is the form in which the rare earths were introduced as constituents in numerous alloys for a variety of applications. A selection of alloys that benefit from rare-earth additions are described below.

1.7.1.1 Ductile Iron

The rare earths played a leading part in the discovery and commercialization of nodular iron (Linebarger and McCluhan 1981). Nodular iron has properties similar to mild steel and is essentially a ductile cast iron. Nodular iron results when the graphite flakes in cast iron are converted to nodules. In the 1940s, it was discovered that spheroidal graphite could be routinely produced in the laboratory in irons containing 0.02% Ce. The rare-earth elements cleanse the metal of elements that prohibit spherical graphite growth, and the compounds they then form provide heterogeneous substrates for graphite nucleation. Nodular iron has good mechanical and foundry properties and is an attractive engineering material, particularly in the automotive industry.

TABLE 1.3
Rare-Earth Application Areas

Application Areas	Subareas, Components, and Devices	Proportion of Total Rare-Earth Consumption in 2010, %
Magnets	Motors	20.8
	Disk drives and disk drive motors	
	Power generation	
	Actuators	
	Microphones and speakers	
	Magnetic resonance imaging (MRI)	
	Anti-lock breaking system	
	Automotive parts	
	Communication systems	
	Electric drive and propulsion	
	Frictionless bearings	
	Magnetic storage disk	
	Microwave power tubes	
	Magnetic refrigeration	
	Maagnetostictive alloys	
Catalysts	Petroleum refining	19.6
	Chemical processing	
	Catalytic converter	
	Diesel additive	
Electronics	Industrial pollution scrubber	
	Display phosphors (CRT, Plasma	7
	Display Panel [PDP], LCD)	
	Medical imaging phosphors	
	Lasers	
	Fiber optics	
Glass	Optical temperature sensors	
	Polishing compounds	24
	Optical glass	
	Ultraviolet (UV)-resistant glass	
	Thermal control mirrors	
Ceramics	Colorizers/decolorizers	
	Capacitors	6
	Sensors	
	Colorants	
Metal alloys	Scintillators	
	Hydrogen storage (NiMH batteries,	18
	fuel cells)	
	Steel	
	Lighter flints	
	Aluminum/magnesium	
	Cast iron	
Superalloys		

(Continued)

TABLE 1.3 (CONTINUED)
Rare-Earth Application Areas

Application Areas	Subareas, Components, and Devices	Proportion of Total Rare-Earth Consumption in 2010, %
Others	Water treatment Fluorescent lighting Pigments Fertilizer Medical tracers Coatings	6

Source: Gschneidner, Jr. K.A., *Material Matters*, 6(2), 2011b.

In the manufacture of nodular iron, rare earths are added as misch metal or mixed rare-earth silicides and not as pure rare-earth metals, mainly due to cost considerations (Davies 1981). Magnesium has emerged as competition for rare earths for graphite nodularization in cast iron, threatening the continued use of misch metal for this purpose (Falconnet 1988).

1.7.1.2 Steels

The deleterious effect of sulfur on the mechanical properties of freshly cast steel is well known. Iron sulfides form and concentrate at the boundaries between the grains of steel formed on solidification. Such steels are very brittle and fracture on working. Addition of rare earths to steel causes the sulfur content to be captured in the form of very stable compounds such as RE₂S₃ or RE₂S₂O. These compounds tend to form globular or spherical inclusions that do not concentrate at the grain boundaries, thus greatly enhancing ductility (Luyckx 1981). The sulfides and oxysulfides are very stable at steel-making temperatures, and unlike other sulfides such as those of manganese, they neither deform nor elongate under processing conditions. As the rare-earth concentration is increased, MnS inclusions are displaced by rare-earth oxysulfides or sulfides. The stability of granular rare-earth sulfides alleviates the detrimental effects of elongated MnS inclusions on toughness. Besides the improvements in the toughness characteristics of high-strength low-alloy (HSLA) steels, rare-earth additions also improve fatigue, creep, and several other mechanical properties (Collins et al. 1961; Linebarger and McCluhan 1981) of steels. The rare earths react quite efficiently with hydrogen in steel and also lower the hydrogen diffusion coefficient.

Rare earths are added to steel as misch metal, rare-earth silicides (RE content, 30%), and alloys such as Fe–Si–10RE, Mg–FeSi–0.1 to 0.2 RE. The effect of rare-earth metals in steels, in whichever form they are introduced, is the same, and the amount of misch metal usually added to ferrous alloys is about 0.1–0.2%. Such small additions do lead to considerable beneficial effects in both nodular iron and steels. Starting in the late 1960s, rare-earth additions to steel in the forms mentioned above became widely prevalent. The practice of adding rare earths to steel was reviewed by Wauby (1978). A few kilograms of misch metal were added to each metric ton

TABLE 1.4
Applications of Rare Earths

Rare Earth	Applications (of the Metal and Its Alloys and Compounds)
Rare earths	Raw material for myriad rare-earth chemicals and functional materials.
Lanthanum	Nickel–metal hydride (NiMH) batteries, phosphors for lighting, fluid-cracking catalysts for petroleum refining, LaNi ₅ for hydrogen gas storage and management, metallurgical alloy additive to cast iron, steel and magnesium alloys, lighter flint, additive to optical glass (for cameras), lanthanum hexaboride ceramic (thermionic emitter) and other specialized ceramic compositions, Department of Defense (DOD) communication devices.
Cerium	Dominant rare earth with maximum number of uses. Polishing agent (for precision optical polishing) of glass, faceplates, mirrors, optical glass, silicon microprocessors, and disk drives; additive to glass; additive to (1) decolorize glass by keeping iron in its ferrous state, (2) block out ultraviolet light (medical glassware and aerospace windows), and (3) suppress discoloration of television glass; prevent polymers from darkening in sunlight; in phosphors, a sensitizer, in a variety of ceramics, including dental compositions and as a phase stabilizer in zirconia-based products; in catalytic converters, a stabilizer for the high-surface-area alumina; a promoter of the water–gas shift reaction; an oxygen storage component; and an enhancer of the NOX reduction capability of rhodium. Cerium is added to the catalyst for the production of styrene from methylbenzene to improve styrene formation; in fluid catalytic cracking (FCC) catalysts containing zeolites to provide both catalytic reactivity in the reactor and thermal stability in the regenerator; in steel manufacturing to remove free oxygen and sulfur by forming stable oxysulfides and by tying up undesirable tramp elements, like lead and antimony, in self-cleaning ovens, carbon-arc lighting, and misch metal.
Praseodymium	Highly valued as a bright yellow pigment for glass and ceramics, used in the scintillator for medical computerized axial tomography (CAT) scans; can partially substitute for neodymium in neodymium–iron–boron magnets for improved magnet corrosion resistance; used in electric vehicle motors and wind turbine generators; additive for high-strength metals; DOD guidance and control systems.
Neodymium	Most famous of the primary applications include neodymium–iron–boron (Nd ₂ Fe ₁₄ B) permanent magnets, indispensable and extensively used in every area of modern technology (both civilian and defense) that relies on superior performance, reliability, and miniaturization. Neodymium has a strong absorption band centered at 580 nm, which is very close to the human eye’s maximum level of sensitivity, making it useful in protective lenses for welding goggles. It was also used in CRT displays to enhance contrast between reds and greens. It is highly valued in glass manufacturing for its attractive purple coloring to glass. Neodymium is included in many formulations of barium titanate, used as dielectric coatings and in multilayer capacitors essential to electronic equipment. Yttrium–aluminum–garnet (YAG) solid-state lasers utilize neodymium because it has optimal absorption and emitting wavelengths. Nd-based YAG lasers are used in various medical applications, drilling, welding, and material processing. Used by DOD in guidance and control systems, electric motors, and communication devices.
Promethium	Beta radiation source; fluid-cracking catalysts.

(Continued)

TABLE 1.4 (CONTINUED)
Applications of Rare Earths

Rare Earth	Applications (of the Metal and Its Alloys and Compounds)
Samarium	Primarily utilized in the production of permanent magnets (SmCo_5 , $\text{Sm}_2\text{Co}_{17}$, Sm-Fe-N), still valued for their ability to function at high temperatures, beyond the operating limits of Nd magnets. Sm–Co magnets are used in precision-guided weapons due to their ability to operate at high temperatures. Used by DOD in guidance and control systems and electric motors.
Europium	Primary use relies on its unique luminescent characteristics. Excitation of the europium atom by absorption of ultraviolet radiation can result in specific energy-level transitions within the atom, creating an emission of visible radiation. In energy-efficient fluorescent lighting, europium provides not only the necessary red but also the blue. Several commercial red phosphors are based on europium for color TV, computer screens, and fluorescent lamps. Its luminescence is also valuable in medical, surgical, and biochemical applications. Combining Eu phosphor compounds with terbium phosphor compounds produces the white light of compact fluorescent lightbulbs, and they are a primary component in the production of T8 and T5 fluorescent tubes. No proven substitute for Eu in fluorescent lamps has been identified. No known substitutes for Eu as a red phosphor in television or liquid crystal display (LCD) screens. Also used as LED phosphor. Eu is also used to dope glasses and plastics for laser production, to investigate biomolecular reactions during drug screening trials, and as a counterfeiting indicator on banknotes. Used by DOD in targeting and weapon systems and communication devices.
Gadolinium	Gadolinium is usable for its high magnetic moment. Mixed with EDTA, it is used as an injectable contrast agent for patients undergoing magnetic resonance imaging. With its high magnetic moment, gadolinium can reduce relaxation times and thereby enhance signal intensity. The particularly stable half-full 4f electron shell with no low-lying energy levels creates applications as an inert phosphor host, for x-ray cassettes, and in scintillated materials for computer tomography. It has a potential application as the functional (magnetocaloric) material in magnetic refrigeration.
Terbium	Terbium is a high-intensity green emitter, primarily used in phosphors, fluorescent lamps, and projection televisions, as YAG (Tb:YAG). Terbium responds efficiently to x-ray excitation and is also as an x-ray phosphor. Terbium alloys were also used in magneto-optic recording films, such as TbFeCo. It is a superior but expensive substitute for dysprosium in neodymium–iron–boron (NdFeB) permanent magnets. Used by DOD in guidance and control systems, targeting and weapon systems, and electric motors.
Dysprosium	Dysprosium is an essential additive in NdFeB for electric vehicle and wind energy applications. Addition of either Dy or terbium (up to 6% of the magnet’s weight) to NdFeB increases the value of intrinsic coercivity or resistance to demagnetization; resistance to demagnetization at higher temperatures also improved. Dy is used in special ceramic compositions based on BaTiO formulations, lasers, chalcogenide sources of infrared radiation, ceramics, nuclear fuel, phosphors, lighting, and catalysts. Used by DOD in guidance and control systems and electric motors.

(Continued)

TABLE 1.4 (CONTINUED)**Applications of Rare Earths**

Rare Earth	Applications (of the Metal and Its Alloys and Compounds)
Holmium	Holmium has the highest magnetic moment of any naturally occurring element. Because of this, it has been used to create the highest known magnetic fields by placing it within high-strength magnets as a pole piece or magnetic flux concentrator. This magnetic property also has value in yttrium–iron–garnet (YIG) lasers for microwave equipment. Holmium lasers at a human-eye-safe 2.08 μm allow its use in a variety of medical and dental applications in both YAG and yttrium–lanthanum–fluoride (YLF) solid state lasers. Has applications as red and yellow pigments in glass and zirconia, and in calibration of γ -ray spectrometers.
Erbium	Erbium has application in glass and ceramic coloring (pink), as an amplifier in fiber optics, and in Er:YAG lasers for medical and dental use. It can neutralize discoloring impurities such as ferric ions and produce a neutral gray shade. It is used in a variety of glass products for this purpose. Lasers based on Er are ideally suited for surgical applications because of its ability to deliver energy without thermal buildup in tissue.
Thulium	Thulium products are mainly used in making crystals and lasers. An important application of thulium in the medical field, and relatively independent of its high cost, is the production of portable x-ray sources. These sources are available for about 1 year, as tools in medical and dental diagnosis as well as to detect defects in inaccessible mechanical and electronic components. This type of sources does not need excessive shielding. Usually, a small cap of lead is enough. Thulium can also be used in magnetic and ceramic materials (ferrite).
Ytterbium	Ytterbium is used in fiber-optic technology and lasers. It has a single dominant absorption band at 985 in the infrared, making it useful in silicon photocells to directly convert radiant energy to electricity. Ytterbium metal increases its electrical resistance when subjected to very high stresses. This property is used in stress gauges for monitoring ground deformations from earthquakes and nuclear explosions. It is also used as in thermal barrier system coatings on nickel, iron, and other transition metal alloy substrates. It is also usable as radiation source for portable x-ray units.
Lutetium	Specialist x-ray phosphors; single-crystal scintillators (baggage scanners, oil exploration).
Yttrium	In ceramics (yttria) for molten metal containment; yttria dispersion for strong alloys [oxide dispersion–strengthened (ODS) alloys, etc.]; yttria-stabilized zirconia in thermal plasma sprays to protect aerospace component surfaces at high temperatures; in fluorescent lighting phosphors, computer displays, and automotive fuel consumption sensors; oxygen and sulfur sensors in molten metals and process gas mixtures; YIG in microwave communication equipment for satellites; YAG with neodymium in lasers; yttrium–barium–copper oxide high-temperature superconductors. Used by DOD in targeting and weapon systems and communication devices.
Scandium	Scandium is mainly used in ceramics, lasers, phosphors, and certain high-performance alloys for the aerospace industry.

of special steel used in the manufacture of an Alaska oil pipeline because misch metal improves the physical properties of steel under arctic conditions. Because of its use in the Alaska pipeline steel, a major increase in demand occurred for misch metal in the period 1971–1978. In spite of the fact that the major consumption of rare earths is in the iron and steel industry, the annual tonnage of steel that is treated with lanthanides had indeed been very small (Haskin and Paster 1979). The use of rare earths in the form of rare-earth silicides or misch metal in steels grew explosively in the 1970s and peaked around 1975. Since then, the market for rare-earth products dropped off, following the availability of cleaner steel and the use of calcium for desulfurization (Falconnet 1988).

1.7.1.3 Superalloys

In the early 1960s, researchers at General Electric discovered that stainless steel containing both aluminum and yttrium possessed exceptional high-temperature corrosion resistance. Beginning then and continuing until about 1975, these alloys were produced for limited application in the nuclear industry (Davies 1981). This alloy, known as *fecralloy* to denote the presence of Fe, Cr, Al, and Y, has since been widely used for the fabrication of furnace-heating elements and has been considered as a replacement for ceramic substrates in emission-control catalysts for the automobile industry. Lanthanum is also used in high-temperature iron-based alloys (Davies 1981). An alloy with 200 ppm lanthanum combines oxidation resistance to 1100°C with good ductility and ease of fabrication.

Superalloys are essentially a class of heat-resistant alloys used in gas turbines, electric generators, jet engine exhaust nozzles, and reaction vessels, and, in general, as materials for use in intense oxidizing environments at high temperatures. Certain rare-earth elements are added to superalloys to enhance their oxidation resistance. Yttrium is the active component in the M–Cr–Al–Y (Fe–Cr–Al–Y stated earlier, Ni–Cr–Al–Y, Co–Cr–Al–Y) family of superalloys. The stability of the alumina–chromia skin that forms on oxidation is enhanced by traces of yttrium. These alloys, even when formed by vapor deposition, form an oxide coating that exhibits remarkable adhesion because yttrium acts to prevent the formation of voids at the oxide/substrate interface. Lanthanum and cerium also play a similar role in certain nickel and cobalt superalloy compositions. Cerium is used in amounts ranging from 100 to 300 ppm in certain high-strength nickel alloys to control sulfur and oxygen. Typically, 200–400 ppm of lanthanum is added in nickel-base and cobalt-base high-temperature alloys for gas turbine service. For example, lanthanum raises the operating temperature of nickel-base Hastelloy-K from 950°C to about 1100°C. Without lanthanum, these alloys exhibit less resistance to cyclic oxidation, and lanthanum probably results in a firmly bound oxide layer. Misch metal in small concentrations (0.03–0.05%) added to electrical-resistance alloys such as Ni–20Cr causes the formation of dense and more adherent surface oxides, leading to a tenfold increase in service life, from 1000 to about 10,000 h. The addition of cerium to the Cu78 high-temperature aerospace alloy (Al–8Fe–4Ce) of Alcoa for enhancing its oxidation resistance was noted as the first major industrial use of cerium metal. Usually, less than 1 wt.% of rare earths added in the form of individual metal leads to dramatic improvements in the performance of these superalloys.

1.7.1.4 Magnesium Alloys

The beneficial effects of the addition of rare earths to magnesium alloys were discovered in the late 1930s by Haughton and Prytherch (1937). Sauerwald (1947) discovered the exceptional grain-refining action of zirconium in magnesium. Murphy and Payne (1947) showed that the rare-earth additives are compatible with zirconium, and enhanced properties could be obtained by incorporating both rare earths and zirconium. Subsequently, zinc (Emley 1966) or silver was also included a desirable additive to these alloys.

At high temperatures, as compared to conventional magnesium alloys, magnesium alloys containing about 3% misch metal and 1% Zr show enhanced creep strength (Kremers 1961). Significantly higher strength at all temperatures was obtained by using Di (Nd + Pr) in place of misch metal as the alloying constituent. The new-generation magnesium alloys contain individual rare earths. One of the two magnesium alloys for use in high-performance engines for aircraft, space rockets, and satellites, possibly as castings, contains 4% zinc and 1% misch metal and can be used in applications seeing temperatures as high as 160°C. The other, which contains 5.5% yttrium, 3.5% other rare earths, and 0.5% zirconium, is stable at temperatures up to 280°C (Jackson and Christiansen 1993). A Mg–Al–Zn–Nd alloy has good corrosion resistance in a saline solution, and a Mg–Y–Nd–Zr alloy was shown to have good corrosion resistance, good castability, and stability up to 300°C. Rare earths refine the grain and improve strength, ductility, toughness, weldability, machinability, and corrosion resistance in the host alloys.

Improving upon the commercially available Mg–Y–Nd–Zr alloy, a lower-weight high-creep-resistance quaternary alloy Mg–Gd–Sc–Mn has been developed by researchers at TU Clausthal, in Germany (Hedrick 2001).

It has also been found that a melt-spun amorphous magnesium alloy containing 10 at.% cerium and 10 at.% nickel has good ductility and, in addition, a tensile fracture strength more than twice as large as conventional optimum age-hardened alloy.

1.7.1.5 Aluminum Alloys

A small amount of yttrium (100 ppm) in combination with zirconium was found to increase (by 50%) the electrical conductivity of aluminum transmission lines (Davies 1981). The addition of misch metal to aluminum-base alloys used for high-tension transmission lines has led to improved tensile strength, heat resistance, vibration resistance, corrosion resistance, and extrudability. An yttrium–magnesium–aluminum alloy has been developed in China for transmission cabling (McGill 1997).

The aluminum alloys 22Si–1MM and 2.5Cu–1.5Ni–0.8Mg–1.2Fe–1.2Si–0.15MM possess good high-temperature properties and fatigue strength and are used in the automobile industry, aircraft, small engine, and other fields. A new aluminum alloy composed of aluminum, iron, and cerium is also under development as a replacement for titanium components in specific applications in the range of 90–315°C. Cerium imparts the required corrosion resistance at elevated temperatures (Jackson and Christiansen 1993). Significant improvements in high-strength Al–Mg and Al–Li alloys have been obtained by the addition of scandium (McGill 1997).

The addition of scandium to aluminum increases the yield strength as it reduces the grain size. The scandium–aluminum alloy has been used in a premier line of

baseball and softball bats. The high-strength alloy allows the bats to have thinner walls, less weight, and greater rebound (Hedrick 1997).

A low-density glassy alloy containing about 90 at.% Al, up to 9 at.% transition metals, and about 5 at.% rare earths has been under development (Kilbourn 1988). The transition metals considered were iron, cobalt, and nickel, and the rare earths were cerium, neodymium, and yttrium. These materials, produced by melt spinning, have extremely high tensile strengths, about twice that of the best crystalline commercial alloy, and good ductility, in addition to low density. These characteristics are attractive for aerospace applications.

An Al–8 wt.% Fe–4 wt.% Ce alloy was made by the rapid solidification (RS) technique of melt spinning and processed further by powder metallurgy techniques. These alloys rely on the rapid gettering of oxygen by the rare earth. The stability of dispersed oxide particles thus formed improves the high-temperature performance of the alloys (Kilbourn 1988), particularly creep resistance, elevated-temperature tensile strength, thermal stability, and corrosion resistance. Compared to the heat-treatable ingot metallurgy products whose elevated-temperature properties are limited to 175°C, the RS Al–Fe–Ce alloys retain good strength even up to 340°C.

About 1–3% misch metal in an aluminum–carbon composite improves the wetting by carbon and, hence, the incorporation of graphite dispersoid in the metal matrix, resulting in a material with improved tensile strength.

1.7.1.6 Titanium Alloys

Yttrium, in concentrations of approximately 200 ppm, was found to improve ductility and ease of fabrication of vacuum arc-melted titanium alloys (Davies 1981). Microalloying of various commercial titanium alloys with rare earths has also resulted in improved strength, stress rupture, and oxidation resistance.

Rapidly solidified titanium alloys (the rare-earth addition, particularly Y, Nd, Er, or Ce, ranged from 1% to 2%) showed improvements by orders of magnitude in high-temperature yield strength, stress rupture life, and creep resistance. The most important of the rare-earth additives have been those with erbium or yttrium (Mahajan and Rama Rao 1988).

1.7.1.7 Copper Alloys

The addition of misch metal or yttrium to oxygen-free high-conductivity (OFHC) copper enhances oxidation resistance without affecting electrical conductivity. For example, the oxidation resistance at 600°C nearly doubled when 0.1 wt.% Y was added to copper.

Misch metal additions have been used to improve the hot workability and deep-drawing characteristics of bronzes containing less than 1 wt.% lead and also the wear resistance of highly leaded bronzes. Adding misch metal in leaded bearing bronze reduced the coefficient of friction by a factor of 4.

1.7.1.8 Zinc Alloys

Misch metal is a constituent in the alloy Galfan (Zn–5% Al–0.05% MM), used in galvanizing baths. This alloy, developed by the International Lead–Zinc Research Organization, is superior with respect to corrosion resistance and permeability to

standard galvanized steel sheets and wire of equal coating thickness and has comparable paintability and weldability properties (Radtke and Herrschaft 1983).

1.7.1.9 Oxide Dispersion–Strengthened Alloys

In oxide dispersion–strengthened (ODS) alloys, the high thermal stability of the rare-earth oxides such as Y_2O_3 and CeO_2 impart desirable properties, like high-temperature strength, creep resistance, and resistance to cyclic corrosive oxidation (Kilbourn 1988). Yttria (0.25–1.3%) is introduced into the nickel–chromium and iron–chromium alloys by mechanical alloying. The mechanical alloying is a high-energy ball-milling process that permits solid-state processing and results in the biggest improvement in properties. After mechanical alloying, the alloy powder is processed by powder metallurgy techniques. The products are high-temperature high-strength ODS alloys, which have found use in gas turbine blades, combustors, and other such applications.

1.7.1.10 Long-Range-Ordered Alloys

Long-range-ordered alloys such as $(Fe,Co)_3V$, $(Fe,Ni)_3V$, and $(Fe,Co,Ni)_3V$ are materials with potential for high-temperature applications. The addition of a small amount of Ce (<0.1%) together with titanium has been found to double the rupture ductility, substantially lower the creep rate, and considerably improve the rupture life of some of these alloys (Mahajan and Rama Rao 1988). In another application, mixtures containing Zr, Ce, and Y oxides of controlled particle morphology are plasma sprayed onto the metal surfaces to create barrier coatings for the protection of the metal substrates against high-temperature degradation.

1.7.2 MAGNETS

Magnets are fascinating materials, and the rare earths share a wonderful relationship with magnets and magnetism.

There are only two naturally occurring magnets. One is the mineral pyrrhotite, and the other is a type of the mineral magnetite. While ordinary magnetite is attracted to a magnetic field like iron and steel are, it does not become a magnet itself. Only a certain variety of magnetite with a particular crystalline structure (a mixture of magnetite and maghemite) has sufficient coercivity to remain magnetized and thus be a permanent magnet (PM). This mineral has been known as a *lodestone* or *loadstone*. It is mostly found at the surface of the earth; not buried at great depth. According to one theory, lodestones were magnetized by the strong magnetic fields surrounding lightning bolts. The ancient Greeks are credited with discovering lodestone, and the first reference to this material dates back to the sixth century BCE. The name *magnet* might have come from lodestones found in the ancient Greek city Magnesia.

King (2012), in a recent article, traced the 270 years of progress in magnet technology by presenting a visual of three magnets that were state-of-the-art materials in the years 1735 (lodestone), 1952 (ferrite), and 1985 (Nd–Fe–B). The picture is reproduced in Figure 1.5. Each magnet shown here produces half a joule of magnetic energy, yet the size has decreased a thousandfold. Another oft-repeated figure of Constantinides (2012a,b), also reproduced in Figure 1.5, demonstrates the dramatic decrease in magnet sizes over a 50-year period that have made possible many of the consumer devices as we know them today.

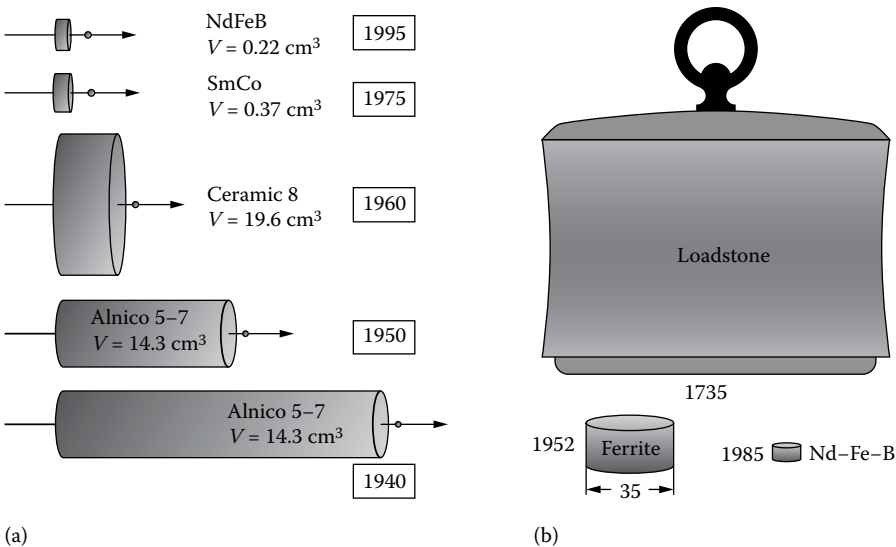


FIGURE 1.5 270 years of progress in magnet technology. (a) Each magnet here produces half a joule of magnetic energy, yet the size has decreased a thousandfold. • Lodestone • ferrite • Nd-Fe-B (b) Relative magnet size to generate 1000 gauss field at 5 mm from the pole face of the magnet. (From King, A., *Rare earth magnet R&D*, The Ames Laboratory, USDOE Iowa State University of Science and Technology, 2012; Constantinides, S., *Material matters*, 2012a; Constantinides, S., *The demand for rare earth materials in permanent magnets*. In *51st Annual Conference of Metallurgists*, 2012a,b.)

A complete listing of all PMs ever developed is given in Table 1.5. Before the 1930s, certain steels were the only PM materials known. Beginning in the 1930s, new PM materials were discovered with great regularity, in an effort to achieve higher remanence (B_r) and energy product ($BH_{\max}$) and greater resistance to demagnetization. The first major breakthrough was the discovery of alnico in Japan in 1931. Alnico underwent improvisation over the next four decades. The hard ferrite magnet was developed in the 1950s and was being widely used by 1960. In the late 1960s, samarium alloyed with cobalt was first used in magnets, and in the 1980s, the cheaper and more powerful neodymium-iron-boron magnets also became available (Wernick 1995). The rare-earth magnets have since become and are set to remain as a major input to clean technologies and high-efficiency consumer and industrial devices (Constantinides 2012b). A consolidated picture of the PMs highlighting the characteristics of the rare-earth magnets that have earned them such adulation in technology is presented in Table 1.6 (Constantinides 2011a). A majority of all the PMs that were ever developed are in production till this date. The status of worldwide production and consumption of the four major PM types—alnico, ferrite, Sm-Co, and NdFeB, over the past 40 years is given in Figure 1.6 (Constantinides 2012a,b). Each PM material apparently has a technocommercial space all for itself. This is depicted in Figure 1.7 (Dent 2012), wherein the magnetic properties provided by the magnets and the temperature limits of their normal operation are given.

TABLE 1.5
Permanent Magnet Development Timeline

Material	First Reported	Reference	BHmax (MGOe)	Hci (Oe)
Carbon steel	c. 1600	Gilbert	0.2	50
Chrome steels	c. 1870	Hadfield	0.3	65
Cobalt steel	1916	Honda et al.	0.9	230
Remalloy	1931	Seljesater	1.1	230
Alnico	1931	Mishima	1.4	490
New KS	1934	Honda et al.	2.0	790
PtCo	1936	Jellinghaus	7.5	4300
Cunife	1937	Neumann et al.	1.8	590
Cunico	1938	Dannöhl and Neumann	1.0	450
Alnico, field treated	1938	Oliver and Shedden	5.5	640
Vicalloy	1940	Nesbitt and Kelsall	3.0	450
Alnico, DG	1948	McCaig, Bemius, Ebeling	6.5	680
Ferrite, isotropic	1952	Went et al.	1.0	1800
Ferrite, anisotropic	1954	Stuijts et al.	3.6	2200
Lodex	1955	Luborsky et al.	3.5	940
Alnico 8	1956	Koch et al.	4.5	1450
Alnico 9	1956	Koch et al.	9.2	1500
RECo ₅	1966	Strnat et al.	16.0	7000
RECo ₅	1970	Benz and Martin	19.0	8000
RE ₂ (Co,Fe,Cu,Zr) ₁₇	1972	Strnat et al.	32.0	25,000
RE ₂ TM ₁₄ B	1984	Koon, Croat, Sagawa (Range of properties)	26.0 35.0	25,000 11,000
RE ₂ TM ₁₄ B	2010	(Numerous) (Range of properties)	30.0 52.0	35,000 11,000

Source: Constantinides, S. The demand for rare earth materials in permanent magnets. In *51st Annual Conference of Metallurgists*, Niagara Falls, Sept. 30–Oct. 3, Met. Soc. of CIM, 2012b.

Sintered magnets of the SmCo₅ type, the first of the rare-earth magnets to be available commercially, possess specific magnetic properties much superior to the well-known and hitherto well-established ferrite and alnico magnets. This is shown by the values in Table 1.6. The intermetallic SmCo₅, because of its hexagonal structure, exhibits a high degree of uniaxial anisotropy, resulting in extremely high coercivity, which, in turn, results in considerably greater energy product. The magnetic strength of Sm–Co compounds is predominantly from the cobalt atoms. Samarium apparently helps define an anisotropic structure *locking* the cobalt moments in place and rendering demagnetization difficult (Molycorp 1993).

The superior properties of rare-earth magnets not only permitted extensive miniaturization in a wide variety of consumer and industrial products but also resulted in performance characteristics hitherto unattainable. Both samarium and cobalt are

TABLE 1.6
Magnet Characteristics—Comparative Values for Major Types

Characteristic	Units	Alnico 5–7	Alnico 9	Ferrite 8	Ferrite 9	SmCo 1:5	SmCo 2:17	NdFeB 33EH	NdFeB 48M	Indicator
Flux density (Br)	Tesla	1.35	1.12	0.39	0.45	0.9	1.1	1.15	1.39	> is better
Energy product (BHmax)	kJ/m ³	60	84	28	37	175	230	230	370	> is better
Resistance to demagnetization (Hci)	kA/m	59	115	245	370	2400	1600	2400	1115	> is better
Usable temperature range	°C	4 K to 520°C	4 K to 520°C	–40 to 150°C	–40 to 150°C	4 K to 520°C	4 K to 520°C	150 K to 200°C	150 K to 100°C	Minimum –40°C to 200°C
Induction change with temperature (RTC of Br)	%/°C	–0.02	–0.01	–0.2	–0.18	–0.045	–0.035	–0.11	–0.12	< is better
Second quadrant normal curve	Shape	Curved	Curved	Straight	Straight	Straight	Straight	Straight	Straight	Straight
Recoil permeability	B/H	2	1.3	1.04	1.04	1.03	1.05	1.04	1.05	~1
Corrosion resistance		Excellent	Excellent	Outstanding	Outstanding	Good	Good	Fair	Fair	Outstanding
Physical strength	MPa	55	55	65	70	120	120	285	285	>50 also “tough”
Electrical resistivity	μΩ·cm	47	50	10 ⁶	10 ⁶	55	90	180	180	> is better
Magnetizing field requirement	kA/m	120	240	480	800	2000	4000	2700	2700	<4000
Coefficient of thermal expansion	%/°C × 10 ^{–6}	11.5	11	10 to 15	10 to 15	7 to 14	11 to 13	7.5 to –0.1	7.5 to –0.1	<15
Approximate current price (relative to NdFeB 33EH)		0.2	0.225	0.04	0.075	0.6	0.5	1	0.75	< is better

Source: Constantinides, S., Rare earth science community help needed for clean energy initiatives, Presentation at the 26th Rare Earth Research Conference (RERC 2011), Santa Fe, New Mexico, June 19–23, 2011a.

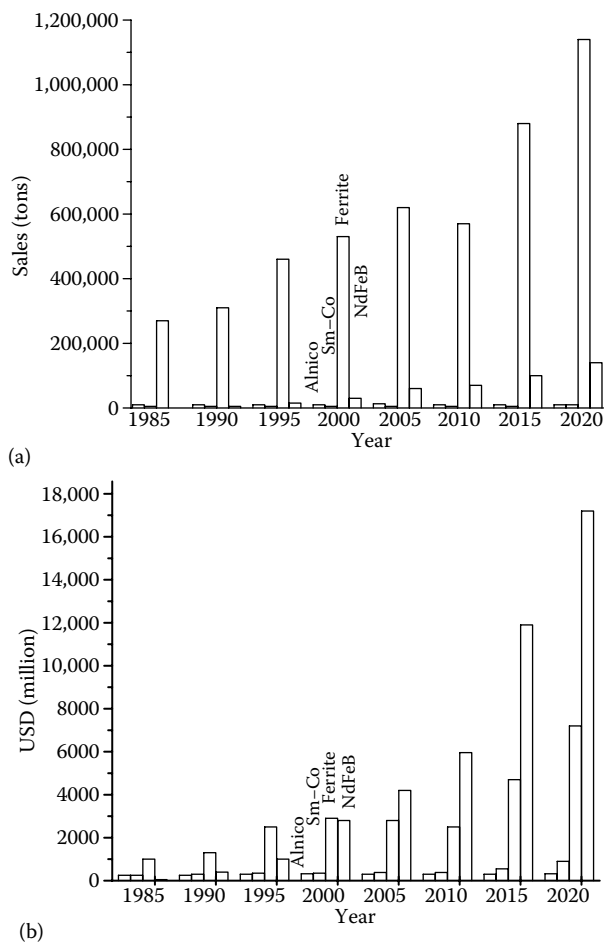


FIGURE 1.6 Permanent magnet sales (a) by volume and (b) by value for the four largest commercially available materials. (From Constantinides, S., The demand for rare earth materials in permanent magnets. In *51st Annual Conference of Metallurgists*, 2012b.)

expensive and limited in supply, and this made the SmCo_5 magnets expensive. The disadvantage of the high cost of samarium was sought to be offset by using misch metal in its place. The use of misch metal offers significant cost reduction, particularly for large-volume applications, such as in electric machinery. The theoretical energy product of PrCo_5 is 30% higher than that of SmCo_5 , but PrCo_5 has substantially weaker anisotropy compared with SmCo_5 (Wallace et al. 1988). Praseodymium, which is more abundant than samarium, was considered to replace Sm in SmCo_5 materials (Kilbourn 1988). While praseodymium addition to samarium raises the strength of the magnet, it also increases corrodibility. Gadolinium is substituted for part of the samarium in temperature-stabilized grades of SmCo_5 , which provide no change in flux output in the range of -40°C to 150°C (Constantinides 2012a,b).

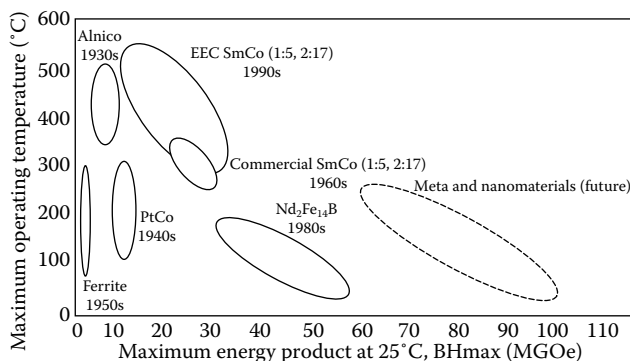


FIGURE 1.7 Operating temperature range for various magnets and their energy products. (From Dent, P.C., *J. Appl. Phys.*, 111: 07A721, 2012.)

A new generation of samarium–cobalt magnets that not only permitted savings in raw material costs but also provided enhanced magnetic properties was based on the 2:17 alloy, $\text{Sm}_2\text{Co}_{17}$. This material was developed between 1969 and 1974. Electron Energy Corporation (EEC) (Dent 2012). In temperature-stabilized grades, gadolinium is substituted for part of samarium. The most widely used of the 2:17 alloys are of the type $\text{Sm}(\text{Co}, \text{Cu}, \text{Fe}, \text{M})_x$, where $\text{M} = \text{Zr}, \text{Hf}, \text{or Ti}$, and x is in the range of 7.0 to 7.85. Higher-temperature grades, for use at over 500°C , have a higher cobalt and reduced-iron content in the magnet composition.

The continuing search for new PM materials has led to the emergence of certain rare earth–iron intermetallic compounds modified by interstitials such as nitrogen and carbon, for example, $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ (Coey et al. 1991b). Interstitial modification has been found to bring advantages, like an increase in Curie temperature and development of a strong uniaxial anisotropy (Collocott et al. 1999). Sm–Fe–N magnets have excellent temperature stability. The material is produced as a powder by mechanical alloying. It is almost always converted to bonded magnets because any attempt to sinter by heating beyond about 450°C will result in the decomposition of the material with the release of nitrogen. For bonded magnets, Sm–Fe–N can have a higher-energy product than anisotropic neo powder. Sm–Fe–N magnets are relatively expensive because of the materials and processes involved (Constantinides 2012a,b Coey and Sun 1990; Wallace and Huang 1992).

The discovery of $\text{Nd}_2\text{Fe}_{14}\text{B}$ (Neo) magnets in 1984 ushered in a new era for the rare-earth transition metal-based PMs. The Nd–Fe–B magnets are high-strength magnets with a magnetic energy of up to 50 MGOe, which is a factor 2.5 times greater than that of SmCo_5 magnets, with high remanence and coercive force. There is a large potential for these magnets because iron, which is cheap and available in abundance (unlike the scarce and costly cobalt), is present as the main constituent (82.4 at.%). Neodymium is also in ample supply, being the third most abundant rare earth and constituting 13% of bastnasite and 18.5% of monazite ores.

Immediately after introduction in the market, the demand for and, hence, production of Nd–Fe–B magnets expanded rapidly, driven primarily by the growth of the personal

computer market. By 1990, 75% of all the Neo magnets were used in hard disk drives of PCs. Hard disk, CD, and DVD drives use small and reliable motors to spin the disks and for positioning the read/write head. The spindle drive motors comprise compression-bonded ring magnets made from melt-spun Magnequench powder. The quantity of magnet material per drive is small (~6 g), but the number of drives made is very large (660 million in 2011). Another important large-scale application in the initial years was the substitution of ferrite magnets with Nd–Fe–B magnets in small electric motors of automobiles, an application pioneered by General Motors. One more major use of Nd magnets was in magnetic resonance imaging equipment. The worldwide production of neodymium magnets was driven initially by the electronic industry (especially the manufacture of computers and portable devices like cell phones) as well as by automotive and industrial applications. The future growth of the Nd magnets will be determined by their use in two major green energy technologies, the use of Nd magnets in windmills and the use of Nd magnets in electric vehicles of all formats.

The main limitation of the Nd–Fe–B magnets is their lower Curie temperature (about 300°C). This leaves the field open for Sm–Co magnets (Curie temperature, 700–900°C) for uses where this property is of major importance. The coercivity of Nd–Fe–B high-strength PMs is enhanced by using Dy as an additive. Dysprosium probably substitutes into the magnetic phase, creating $\text{Nd}_{2-x}\text{Dy}_x\text{Fe}_{14}\text{B}$ with higher anisotropy (hence higher coercivity) than the unsubstituted material (Molycorp 1993). Even below the Curie temperature, the high-temperature performance of Nd magnets has been an issue of concern. The situation is depicted in Figure 1.8. Substitution of Dy results in improvement, but above 150°C, the samarium magnets have a superior energy product.

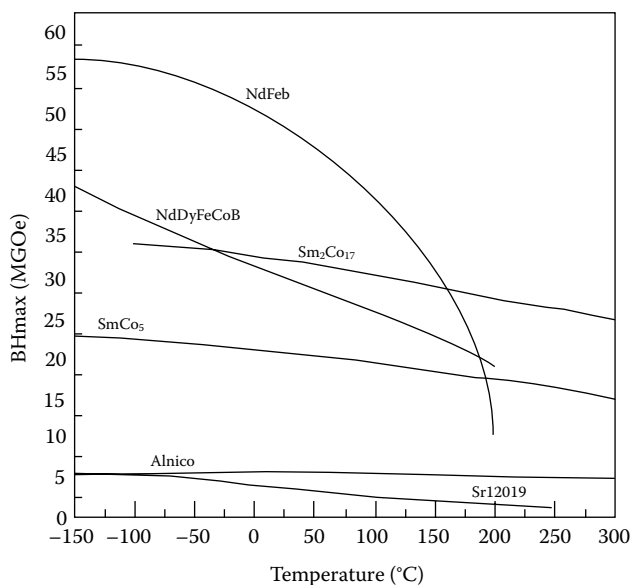


FIGURE 1.8 The temperature performance of the maximum energy product as a function of temperature for many common commercial magnets and some promising alternatives. (From Kramer, M.J. et al., *JOM*, 64(7): 752–763, 2012.)

Rare earth–Transition Metal™ permanent magnets are considered essential to many military weapon systems. Sm–Co magnets retain their magnetic strength at elevated temperatures and are preferred for military technologies such as precision-guided missiles, smart bombs, and aircraft. The superior strength at lower temperatures and, hence, smaller and lighter NdFeB magnets are also preferred in defense weapon systems.

The characteristics possible in rare-earth magnets have revolutionized magnet design in recent years, most notably in the production of high-performance electric motors, which convert electricity into mechanical motion, and electric generators, which, operating in reverse, convert mechanical motion into electricity.

As a pollution-free, energy-efficient alternative, electric drive systems are or could be part of a range of transport vehicles starting from the smallest, motor assisted bicycles; through cars, SUVs, and trucks; to even large mining and earth-moving equipment. Presently, the main commercial products using electric drives, exclusively or with an internal combustion engine, are electric bicycles, hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and all electric vehicles (AEVs). The motor size in a typical electric bicycle is less than 1 kW, compared to a 55 kW traction motor in a Toyota Prius (HEV). The per-unit usage of magnet material ranges from 60 g for bicycles to 350 g for high-power scooters and 2400 g for the passenger car. PM motors (PMMs) and generators (PMGs) are used in, for example, Prius-class HEVs, to power the vehicle as well as to recapture energy associated with braking, respectively. Each Prius HEV requires an estimated 1 kg of Nd + Pr and perhaps 100–200 g of Dy in the various magnets required for operation. The Neo magnet material for use in these thus contains 4–10% Dy, primarily due to the high temperature of the application coupled with localized high demagnetization fields. Almost all mass-produced HEVs and electric vehicles (EVs), which include PHEVs and all-electric vehicles, use rare-earth PMs in the motors that propel them during electric drive operation. In PHEVs and HEVs, a gasoline engine (or generator) and an electric motor are constrained in size and weight to fit within a tight engine compartment, limiting the choice of motor size and operating characteristics. AEVs have no gasoline engine, which allows more flexibility and alleviates space constraints, making it easier to cool the motor.

Electric energy generation via wind power has been an industry holding out many possibilities as a renewable, nonpolluting alternative for nearly three decades. Wind turbine generators convert wind energy into electricity, and neodymium–iron–boron rare-earth PMs are used in wind turbines. Wind power as a viable technology alternative for electricity generation has been increasingly implemented all over the world in the past decade, and during this time, there has been a gradual progression toward larger, more powerful wind turbines. Permanent Magnet Generators (PMGs) used in megawatt-scale, next-generation wind turbines eliminate massive mechanical gearboxes and other components that are subject to reliability issues. The magnets in these large turbines contain an estimated 150–200 kg of Nd + Pr and perhaps 20–35 kg of Dy, per megawatt of generating capacity. Thus, larger turbines are more likely to use rare-earth PMs, to dramatically reduce the size and weight of the generator compared to non-PM designs such as induction or synchronous generators. Another trend is toward turbines equipped with electricity

generators that run at slower speeds, allowing better coupling with the turbine rotor. For a given power rating, slow-speed turbines require larger PMs. Constantinides (2011a) estimated that presently, direct-drive turbines require 600 kg of PM material per megawatt, which translates to several hundred kilograms (~310 kg REO) of rare-earth content per megawatt. The estimates for the future, given by him, reduced the quantity of PM material required per megawatt to 400 kg, possibly anticipating the development of a superior Nd magnet and/or a superior design for the windmill generator.

The rare-earth PM designs still make up only a small percentage of the market for wind turbines, as of now, and the situation will be changing, in all likelihood, in favor of greater use of the rare earths in the world wind power sector. Wind power requirements for rare earths depend on the total installed wind power (megawatts) and the fraction of this total that use PM generators. The numbers listed in Table 1.7 are very informative in this context. The table concludes with an estimate for not only the neodymium but also the critically important dysprosium additive.

In any case, possible uncertainties in the future supply of critically important rare-earth materials Nd and, particularly, Dy have also accelerated the development of alternatives like the superconducting generator turbines, which do not use PMs and which show promise for turbines in the 10 MW+ range. American Superconductor has been developing a 10 MW Sea Titan turbine prototype that uses a direct-drive high-temperature superconducting generator (Constantinides 2012a,b).

1.7.3 TERFENOL

Magnetostriction is a property exhibited by certain materials, and these materials are known as magnetostrictive materials. A magnetic field applied to a magnetostrictive material makes it expand or contract, and conversely, when stress is applied to the magnetostrictive material, a magnetic pulse is generated. The property of magnetostriction was discovered in 1971, but it took another 15 years before commercial application of the phenomenon became possible with the development of suitable materials (Jiles 1994). Iron alloys of rare earths such as Tb, Sm, and Dy exhibit properties of very large magnetostriction. The Laves-phase alloy $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_{1.9}$ (terfenol-D), in particular, shows outstanding magnetostrictive properties. Terfenol-D was initially developed in the 1970s by the Naval Ordnance Laboratory (NOL) and named after terbium (TER), iron (Fe), and NOL; *D* comes from *dysprosium*. The technology for manufacturing the material was developed in the 1980s at Ames Laboratory under a US Navy-funded program (Clark 1979). The magnetostriction in an applied field exhibited by terfenol is approximately 100 times larger than that of nickel, the well-known metal exhibiting magnetostriction. Terfenol changes dimension in a magnetic field instantaneously, and this effect is essentially at the heart of advanced transducers and micropositioners. Its initial application was in naval sonar systems. Terfenol is also used in areas of high-power actuators, acoustic devices, broadband sonar devices, micropositioners, fluid control valves, and micropumps (Gschneidner and Daane 1988; McGill 1997). Terfenol-D was also slated for use as the smart material to control fluid flow in natural-gas fuel injection in light-duty diesel engines (Hedrick 2000).

TABLE 1.7
The Windmill Story

Country	Cumulative Installed Capacity as of End of 2010, MW	Installed during 2010			Forecast for Installation during 2020		
		Installed MW	% PM Generators	Neo Magnets Required, Metric Tons (Average, 600 kg/MW)	Installed MW	% PM Generators	Neo Magnets Required, Metric Tons (Average, 400 kg/MW)
China	44,733	18,928	95%	10,789	10,000	90%	3600
USA	40,180	5115	10%	307	15,000	75%	4500
India	13,065	2139	5%	64	5000	75%	1500
Spain	20,676	1516	5%	45	3000	75%	900
Germany	27,214	1493	5%	45	1500	75%	450
France	5660	1086	5%	33	1500	75%	450
UK	5204	962	5%	29	1000	75%	300
Italy	5797	948	5%	28	800	75%	240
Canada	4009	690	5%	21	800	75%	240
Sweden		604	10%	36	500	75%	150
Rest of world	30,501	4785	5%	144	15,000	75%	4500
Total	197,039	38,265		11,540	54,100		16,830
Dy requirement at 4.1 wt. %				473			690
Nd requirement at 27.5 wt. %				3174			4628

Source: Constantinides, S., Rare Earth Materials, In *SMMA Management Conference*, Spring, May 10–12, San Diego, CA, 2011.

Dysporium–terbium–iron magnetostrictive alloys are also being developed for use as actuators to allow precision positioning of the next-generation space telescope (NGST) (Hedrick 1998). Incidentally, NGST would have 6 to 12 times the surface area of the Hubble space telescope.

1.7.4 MAGNETIC REFRIGERATION

Gadolinium metal and alloys have been considered as the working substance in magnetic refrigeration cycles (Hashimoto et al. 1981). The underlying principle of magnetic refrigeration is that a gadolinium-based solid heats up in a strong magnetic field and cools when removed from the field. This system works even at room temperature but has the greatest prospects in cryogenic applications. Initially, GdPd was used, and later, the gadolinium–aluminum garnet (GAG) single crystal and intermetallics ($\text{Dy}_{0.5}\text{Er}_{0.5}$) Al_2 and TbNiO_2 were used as magnetic refrigerants for cooling to as low as 4 K. The refrigerator using the magnetic refrigerant is called the active magnetic regenerative magnetic refrigerator (AMR-MR) (Gschneidner and Pecharsky 2006). The main advantages of the magnetic refrigerator are the compactness and large refrigeration power per unit volume. It is also reliable, vibration free, and more efficient than most cryogenic cooling systems, particularly below liquid nitrogen temperature (77 K).

Gschneidner et al. (1999) have reported two major breakthroughs in magnetic refrigeration. They successfully demonstrated that sub-room-temperature magnetic refrigeration is a viable and competitive technology vis-à-vis conventional gas-cycle compression/expansion refrigeration. In a laboratory prototype refrigerator using 3 kg of Gd spheres as magnetic refrigerant in a magnetic field of 5 T, they achieved a cooling power of 600 W, operating at a maximum temperature span of 30 K, while running the apparatus for more than 1200 h over a 10-month period. They also reported the discovery of the giant magnetocaloric effect (MCE) materials $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$, which have MCEs ranging from 25% to 200% better than the known prototype magnetic refrigerants such as gadolinium. As an added attraction, their Curie temperatures are tunable from 40 to 290 K by changing the Si–Ge ratio in this material. These new materials can make magnetic refrigeration more efficient. Refrigeration systems based on the new material can have applications in home and automobile air-conditioning and in household appliances like refrigerators, freezers, and ice makers (Hedrick 1997).

Magnetic refrigeration has great potential for improving the energy efficiency of the refrigeration process using rare-earth PMs. Before this technology can capture a significant share of the refrigeration market, issues like the timeline for commercialization, projected demand, and material intensity of the commercial products need to be sorted out.

1.7.5 CERAMICS

Rare-earth oxides, particularly ceria and yttria, are used as sintering aids in powder metallurgical fabrication due to their ability to eliminate weakening voids (Jackson and Christiansen 1993). For instance, during the sintering of silicon nitride, the Si–Y–O–N liquid phase is formed. On cooling, the nitride grains regroup, the yttrium