

# **HIGH TEMPERATURE MATERIALS and MECHANISMS**



**Edited by  
Yoseph Bar-Cohen**

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## Preface

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High-temperature materials and mechanisms are critical technologies for pushing the boundaries of human capabilities. The use of high-temperature materials is dated as far back as the beginning of human civilization. As early as humans started working with fire and heat, they have used materials that can sustain high temperatures. Initially, the primitives used rocks to handle fire that they applied for cooking and heating. With time, the applications were expanded to making tools that were processed and used at high temperatures. It is interesting to note that the human ability to process and handle materials has improved considerably with their advancement in melting high-temperature materials. During the Stone Age, humans were not able to smelt any ore, whereas during the Bronze and Iron Ages they were able to smelt bronze and iron, respectively, as well as produce artifacts from them. The Industrial Revolution led to an enormous rise in applications and requirements for increased capability and operational safety.

At the end of the nineteenth century, some of the important applications that emerged include the steam turbine, while in the early part of the twentieth century the filament lamp and the combustion engine were developed, and these developments have been followed by jet engines around the 1940s and the space shuttle engine in the 1980s. Steel alloys were introduced at the end of the nineteenth century, followed by stainless steel and nickel-chrome alloys in the beginning of the twentieth century, and these alloys had a major impact on the applications of high-temperature materials. Today, the selection of high-temperature materials has been widened to such metal alloys as refractory metals, super-alloys, and titanium alloys. Other materials that are being used include certain ceramic materials, carbon/carbon composites, metal matrix composites, and many others.

Generally, in materials science the term *high temperature* is defined as the temperature that is equal to, or greater than, about two-thirds of the melting point of a solid. However, there are other definitions too, including application-based definitions such as heat resistance (e.g., strength and corrosion resistance) above 500°C. Since increasing the temperature decreases the material strength, they need to have high strength at the required operating temperatures with a safety margin in order to make these materials effective and economical. High-temperature materials need to be resistant to such causes of damage as oxidation and corrosion, which are accelerated with the increase in temperature. Generally, extrapolating the material properties and chemical behavior do not correlate with the high-temperature data. Specifically, as the temperature rises, chemical reactions become pronounced and thermodynamic properties determine the reactivity rather than kinetics. Also, there are various effects that take place, including disorder of the material structure.

It is interesting to follow the parallel development of materials and the resulting industrial applications. Specifically, the driver of engineering requirements at the end of the nineteenth century has been the availability of materials and their processing, including powder metallurgy, casting, and vacuum melting. The availability of compatible materials is critical to the ability to develop high-temperature-related technologies such as high-speed airplanes and rockets that can reach 5 Mach and beyond having surface temperature that rises above 500°C. Besides the capability of the materials and structures to sustain high temperatures without irreversible changes and degradation of the properties, it is also necessary to have effective structural designs that allow for efficient heat

dissipation, transfer of the associated high heat fluxes, and the ability to sustain the related thermal conditions.

This book includes Chapters 1 through 5 that cover subjects of high-temperature materials and mechanisms from many angles, including the chemistry and thermodynamics, overview of the various materials, including refractory metals, ceramics and composites for high-temperature structural and functional applications, and adhesives and bonding and their failure causes. Chapters 6 through 8 cover the topics of processes, materials characterization methods, and their nondestructive evaluation and health monitoring. The application of high-temperature materials to actuators and sensors is described in Chapters 9 through 15, including electromechanical materials, such as piezoelectric, thermo-acoustics materials, shape memory and super-elastic alloys, thermoelectric materials drilling mechanisms, as well as electronics. Further, Chapters 16 and 17 cover sensor design challenges and various high-temperature materials and mechanisms applications and challenges.

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## **Chapter 1**

Ted Iskenderian, Jet Propulsion Laboratory (JPL)/Caltech, Pasadena, California

Yiannis Pontikes, Department of Metallurgy and Materials Engineering, KU Leuven, Belgium

## **Chapter 2**

Elizabeth J. Opila, Department of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia

William T. Petuskey, Arizona State University, Tempe, Arizona

## **Chapter 3**

James Gordon Hemrick, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Vilupanur A. Ravi, California State Polytech University, Pomona, California

Mark L. Weaver, University of Alabama, Tuscaloosa, Alabama

Eric Wuchina, Office of Naval Research (ONR), Arlington, Virginia

## **Chapter 4**

John Bishopp, Star Adhesion Limited, Cambridge, UK

Lucas F. M. da Silva, Editor in Chief of *The Journal of Adhesion*, University of Porto (FEUP), Portugal

Linda Del Castillo, Jet Propulsion Lab (JPL)/Caltech, Pasadena, California

Erol Sancaktar, University of Akron, Ohio

## **Chapter 5**

Sebastien Dryeopondt, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Paul Gannon, Montana State University, Bozeman, Montana

Brian Gleeson, University of Pittsburgh, Pittsburgh, Pennsylvania

Bryan Harder, NASA's Glenn Research Center, Cleveland, Ohio

## **Chapter 6**

William Fahrenholtz, Missouri University of Science and Technology, Rolla, Missouri

Yiannis Pontikes, Department of Metallurgy and Materials Engineering, KU Leuven, Belgium

Eric Wuchina, Office of Naval Research, NSWCCD, W. Bethesda, Maryland

**Chapter 7**

Vince Crist, Nanolab Technologies, Milpitas, California

Doreen D. Edwards, North Carolina State University, Raleigh, North Carolina

Kip O. Findley, Colorado School of Mines, Golden, Colorado

**Chapter 8**

Ali Abdul-Aziz, NASA Glenn Research Center and Cleveland State University,  
Cleveland, Ohio

Edward Ecock, Consolidated Edison Company, New York, New York

Darby B. Makel, Makel Engineering, Inc., Chico, California

Subhasish (Subh) Mohanty, Argonne National Laboratory, Lemont, Illinois

Philip G. Neudeck, NASA Glenn Research Center, Cleveland, Ohio

Don J. Roth, NASA Glenn Research Center, Cleveland, Ohio

**Chapter 9**

Iqbal Husain, North Carolina State University, Raleigh, North Carolina

Ted Iskenderian, Jet Propulsion Laboratory (JPL)/Caltech, Pasadena, California

Robert Troy, Jet Propulsion Laboratory (JPL)/Caltech, Pasadena, California

**Chapter 10**

Troy Y. Ansell, Oregon State University, Corvallis, Oregon

David Cann, Oregon State University, Corvallis, Oregon

Dragan Damjanovic, Institute of Materials, School of Engineering, EPFL, Lausanne,  
Switzerland

Xiaoning Jiang, North Carolina State University, Raleigh, North Carolina

**Chapter 11**

Wael Akl, Faculty of Engineering, Ain Shams University, Cairo, Egypt

Hyeong Jae Lee, Jet Propulsion Laboratory (JPL)/Caltech, Pasadena, California

Ji Su, NASA Langley Research Center (LARC), Langley, Virginia

**Chapter 12**

Alexander Czechowicz, Ruhr-University, Bochum, Germany

Eugenio Dragoni, University of Modena and Reggio Emilia, Italy

Osman E. Ozbulut, University of Virginia, Charlottesville, Virginia

**Chapter 13**

Sabah K. Bux, Jet Propulsion Laboratory (JPL), Pasadena, California

Jeff Sakamoto, Michigan State University, East Lansing, Michigan

Eric Toberer, Colorado School of Mines, Golden, Colorado

Rama Venkatasubramanian, RTI International, Research Triangle Park, North Carolina

**Chapter 14**

George Cooper, University of California at Berkeley, Berkeley, California

Timothy J. Szwarc, Department of Aeronautics and Astronautics, Stanford University, California

**Chapter 15**

Michael Pecht, University of Maryland, College Park, Maryland

Leon M. Tolbert, University of Tennessee, Knoxville, Tennessee

Fred (Fei) Wang, University of Tennessee, Knoxville, Tennessee

**Chapter 16**

Carl W. Chang, NASA Glenn Research Center, Cleveland, Ohio

Liang-Yu Chen, NASA Glenn Research Center, Cleveland, Ohio

Michael Iten, Marmota Engineering AG, Zürich, Switzerland

David Parks, Idaho National Laboratory, Idaho Falls, Idaho

Bernhard R. Tittmann, Pennsylvania State University, University Park, Pennsylvania

**Chapter 17**

Josephine Aromando, Consolidated Edison Company, New York, New York

Robert D. Cormia, Foothill College, Los Altos Hills, California

Somrah, Dowlatram, Consolidated Edison Company, New York, New York

Edward Ecock, Consolidated Edison Company, New York, New York

Jeff Hall, Jet Propulsion Laboratory (JPL)/Caltech, Pasadena, California



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## Editor

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**Dr. Yoseph Bar-Cohen** is a supervisor of the Advanced Technologies Group (<http://ndea.jpl.nasa.gov/>) and a senior research scientist at the Jet Propulsion Lab/California Institute of Technology, Pasadena, California. In 1979, he earned a PhD in physics from the Hebrew University, Jerusalem, Israel.

His research is focused on electro-mechanics, including planetary sample-handling mechanisms, novel actuators that are driven by such materials as piezoelectric and EAP (also known as artificial muscles), and biomimetics. Using ultrasonic waves in composite materials, he discovered the polar backscattering (1979) and leaky lamb waves (1983) phenomena. He (co)edited and (co)authored 8 books, coauthored over 360 publications, co-chaired 44 conferences, and has 22 registered patents. His notable initiatives include challenging engineers and scientists worldwide to develop a robotic arm driven by artificial muscles to wrestle with

humans, and he held contests in 2005 and 2006.

For his contributions to the field of artificial muscles, *Business Week* named him in April 2003 one of five technology gurus who are “Pushing Tech’s Boundaries.” His accomplishments earned him two NASA Honor Award Medals, two SPIE’s Lifetime Achievement Awards, Fellow of two technical societies—ASNT and SPIE, as well as many other honors and awards.



---

## *Contributors*

---

**Grigory Adamovsky**  
NASA Glenn Research Center  
Cleveland, Ohio

**Osama Aldraihem**  
Department of Mechanical Engineering  
King Saud University  
Riyadh, Saudi Arabia

**Masood Taheri Andani**  
Dynamic and Smart Systems Laboratory  
University of Toledo  
Toledo, Ohio

**Mircea Badescu**  
Jet Propulsion Laboratory (JPL)/Caltech  
Pasadena, California

**Xiaoqi Bao**  
Jet Propulsion Laboratory (JPL)/Caltech  
Pasadena, California

**Yoseph Bar-Cohen**  
Jet Propulsion Laboratory (JPL)/Caltech  
Pasadena, California

**Amr Baz**  
Department of Mechanical Engineering  
University of Maryland  
College Park, Maryland

**Linfeng Chen**  
Department of Electrical Engineering  
University of Arkansas  
Fayetteville, Arkansas

**Sang H. Choi**  
NASA Langley Research Center  
Hampton, Virginia

**Robert D. Cormia**  
Department of Engineering  
Foothill College  
Los Altos Hills, California

**R. Peter Dillon**  
Jet Propulsion Laboratory (JPL)/Caltech  
Pasadena, California

**Mohammad Elahinia**  
Dynamic and Smart Systems  
Laboratory  
University of Toledo  
Toledo, Ohio

**Jeffrey W. Fergus**  
Wilmore Laboratory  
Auburn University  
Auburn, Alabama

**Olivia A. Graeve**  
Department of Mechanical and  
Aerospace Engineering  
University of California, San Diego  
La Jolla, California

and

Kazuo Inamori School of Engineering  
Alfred University  
Alfred, New York

**Andrew Gyekenyesi**  
Ohio Aerospace Institute  
Cleveland, Ohio

**Christoph Haberland**  
Dynamic and Smart Systems  
Laboratory  
University of Toledo  
Toledo, Ohio

**Wesley P. Hoffmann**  
Air Force Research Laboratory  
Edwards, California

**Gary Hunter**  
NASA Glenn Research Center  
Cleveland, Ohio

**Nathan S. Jacobson**

NASA Glenn Research Center  
Cleveland, Ohio

**James P. Kelly**

Kazuo Inamori School of Engineering  
Alfred University  
Alfred, New York

**Hyun Jung Kim**

National Institute of Aerospace  
Hampton, Virginia

**Matthew M. Kropf**

The Energy Institute  
University of Pittsburgh at Bradford  
Bradford, Pennsylvania

**Nishant Kumar**

Honeybee Robotics Spacecraft Mechanisms  
Corporation  
Pasadena, California

**Hyeong Jae Lee**

Jet Propulsion Laboratory (JPL)/Caltech  
Pasadena, California

**Jungmin Lee**

Department of Electrical Engineering  
University of Arkansas  
Fayetteville, Arkansas

**John D. Lekki**

NASA Glenn Research Center  
Cleveland, Ohio

**Zhenxian Liang**

Oak Ridge National Laboratory  
Knoxville, Tennessee

**Shyh-Shiuh Lih**

Jet Propulsion Laboratory (JPL)/Caltech  
Pasadena, California

**Gyanesh N. Mathur**

Department of Electrical Engineering  
University of Arkansas  
Fayetteville, Arkansas

**Alexandra Navrotsky**

Peter A. Rock Thermochemistry  
Laboratory  
University of California, Davis  
Davis, California

**Mostafa Nouh**

Department of Mechanical  
Engineering  
University of Maryland  
College Park, Maryland

**Sulata Kumari Sahu**

Peter A. Rock Thermochemistry  
Laboratory  
University of California, Davis  
Davis, California

**Stewart Sherrit**

Jet Propulsion Laboratory (JPL)/Caltech  
Pasadena, California

**Thomas R. ShROUT**

Materials Research Institute  
Pennsylvania State University  
University Park, Pennsylvania

**James L. Smialek**

NASA Glenn Research Center  
Cleveland, Ohio

**Vijay K. Varadan**

Department of Electrical Engineering  
University of Arkansas  
Fayetteville, Arkansas

**Mark Woike**

NASA Glenn Research Center  
Cleveland, Ohio

**Kris Zacny**

Honeybee Robotics Spacecraft Mechanisms  
Corporation  
Pasadena, California

**Shujun Zhang**

Materials Research Institute  
Pennsylvania State University  
University Park, Pennsylvania

# 1

---

## *Introduction*

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Yoseph Bar-Cohen

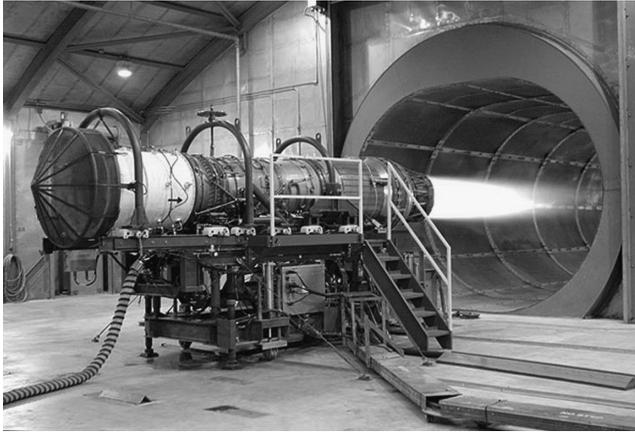
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### 1.1 Introduction

As early as humans started working with fire and heat, they have been using materials that can sustain high temperatures. Initially, the primitives used rocks, which they picked from their neighborhood. As they became more capable in controlling the heat that they produced and the related applications, increasingly efforts were made to control the properties of the produced materials and the performance of the structures that were made. The applications have grown from preparing food and heating their living areas to sophisticated processing methods at higher temperatures as well as applications that involve extreme thermal conditions. Today, the selection of high-temperature materials (Chapter 3) has been widened to such metal alloys as refractory metals, stainless steels, superalloys, and titanium alloys. Other materials that are being used include certain ceramic materials, carbon–carbon composites, metal matrix composites (MMC) and many others. Applications of high-temperature materials include aircraft jet engines (see example of an aircraft fighter jet engine in Figure 1.1), nuclear reactors, and industrial



**FIGURE 1.1**

A Pratt & Whitney F100 turbofan engine for the F-15 Eagle being tested at an Air National Guard base in Florida. The tunnel behind the engine has the functions of allowing the exhaust gases to escape and muffling noise. (From Wikimedia Commons, <http://en.wikipedia.org/wiki/File:Engine.f15.arp.750pix.jpg>; <http://upload.wikimedia.org/wikipedia/commons/2/2e/Engine.f15.arp.750pix.jpg>.)

gas turbines. Also, such materials are used in furnaces and ducts, as well as electronic and lighting devices.

Generally, in materials science the term high temperature is defined as the temperature that is equal to, or greater than, about two-thirds of the melting point of a solid (Spear et al., 2006). However, there are other definitions, too, including application-based ones as well as indicating materials that are used for their heat resistance (e.g., strength and corrosion resistance) above 500°C as described by Meetham and Van de Voorde (2000). Since increasing the temperature decreases the material strength, in order to make them effective and economical, they need to have high strength at the required operating temperatures with a safety margin. High-temperature materials need to be resistant to the related causes of damage including oxidation and corrosion, which are accelerated with the increase in temperature (Chapter 5). Generally, extrapolating the material properties and chemical behavior do not correlate with the high-temperature data (Chapter 2). Specifically, as the temperature of materials rise, chemical reactions become pronounced and thermodynamic properties determine the reactivity rather than kinetics. As the temperature increases, there are various effects that take place including disorder of the material structure.

---

## 1.2 Historical Perspective

The use of high-temperature materials is dated as far back as the very ancient historic years of the start of humans' civilization. Initially, heat was used for cooking and overcoming cold weather but with time the applications expanded to processing extremely high-temperature materials and their use at harsh conditions. It is interesting to note that the eras of technologies that are used to date humans' ability to handle materials is based on their evolved ability to melt high-temperature ones. This includes the Stone Age where

humans were not able to smelt any ore, whereas the Bronze and Iron Ages where humans were able to smelt bronze and iron, respectively, as well as produce artifacts from them. The industrial revolution led to enormous rise in applications and requirements for increased capability and operation safety of both the fabrication of the materials and their usage. Further, new materials were introduced and improved processes were developed for their fabrication and treatment to enhance their strength and durability (Chapters 2 and 6).

Some of the applications that emerged include the development of the steam turbine at the end of the nineteenth century, while filament lamps, combustion engine, and petrochemical industry in the early twentieth century were followed by the development of the jet engine around the 1940s and the Space Shuttle engine in the 1980s (see photo of the space shuttle Atlantis and its three main engines in Figure 1.2). The development of the steel alloys at the end of the nineteenth century as well as the stainless-steel (Brearley, 1913) and the nickel–chrome alloys (Crawford, 1959) in the beginning of the twentieth century had major impact on the application of high-temperature materials. The carbon–carbon composites (Savage, 1993) were developed around 1970.

It is interesting to follow the parallel development of materials and the resulting industrial applications. Specifically, the driver of requirements at the end of the nineteenth century has been the powering of ships and it led to the development and advancements in steam turbines/engines. The development of the gas turbine has benefited greatly from the use of nickel superalloys (Sims, 1987), which were developed around the 1940s. These



**FIGURE 1.2**

The Space Shuttle engine emitted significant level of heat and the temperature rose significantly during launch. This figure shows close-up of the three main engines of the space shuttle Atlantis that launched the shuttle into space. Because the engine burns hydrogen and oxygen, it emits steam through its exhaust. (From NASA/Rusty Backer and Michael Gayle. [http://www.nasa.gov/mission\\_pages/shuttle/flyout/ssme.html](http://www.nasa.gov/mission_pages/shuttle/flyout/ssme.html); high resolution: [http://www.nasa.gov/images/content/502050main\\_ssme\\_firing.jpg](http://www.nasa.gov/images/content/502050main_ssme_firing.jpg))

turbines were used to drive electric power-generating plants and later, jet aircraft. The use of metal alloys with various additives led to substantial improvement of the properties of the available high-temperature materials, including the corrosion resistance of nickel-chrome that was achieved by adding aluminum and titanium. Various manufacturing processes were introduced to improve the available high-temperature materials and these include the use of powder metallurgy, casting, and vacuum melting.

The availability of compatible materials can be critical to the ability to develop high-temperature-related technologies such as high-speed airplanes and rockets that reach speeds of several Mach (Martelluci and Harris, 1991). Specifically, the issue for reaching 5 Mach and beyond is the rise in surface temperature above 500°C, which initially causes large stresses and vaporization of the surface material (fast ablation). Besides the capability of the materials and structures to sustain the high temperatures without irreversible changes and degradation of the properties, it is also necessary to have effective structural design that allows for efficient heat dissipation, transfer of the associated high heat fluxes and the ability to sustain the related thermal conditions. Generally, MMC and titanium alloys are used in structures that need to operate in the range from 300 to about 1000°C and they are selected for their being light weight and easy to manufacture (Tenny et al., 1988). Such alloys as the 6Al-4 V titanium and AM-350 CRES steel have high strength properties, however they tend to fail above 400°C (Jenkins and Landis, 2003). For temperatures above 1000°C, such materials as ceramics and carbon-carbon composites are used.

---

### **1.3 Need for High-Strength High-Temperature Materials**

Generally, there is a need for materials that are capable of being applicable at higher temperatures than available and their development can benefit many industries. For example, significant increase can be reached in the efficiency of pulverized coal power plants that operate under ultra-supercritical conditions (Meetham and Van de Voorde, 2000). Since the material strength degrades with the rise in temperature, the applicability of high strength materials is limited to the requirements of the developed structure. Titanium metal matrix unidirectional composite with SiC reinforcement has strengths as high as over 1400 MPa, but the application of this material is limited to the range of about 500°C. On the other hand, for applications in the range of 1500°C, one can use refractory metals with strength that is less than about 100 MPa or carbon/carbon with strength above 350 MPa. Besides the loss of strength as a function of temperature, one needs to take into account the ability of the material to sustain accelerated oxidation and other degradation effects that may be involved with the exposure to high temperatures.

Continually, new high-temperature materials and alloys are reported (Chapter 3). When new materials emerge from research and development with highly attractive and desirable properties, they are not immediately used in engineering applications. It is essential to identify their disadvantages and to minimize them with proper precaution and attention to the critical issues that are identified. Examples include the recognition by aerospace engineers that titanium is a lightweight, high-temperature material with potential applications to supersonic aircraft structures. However, attention is needed to developing effective processing, thermal treatment, adhesion, welding, and others as well as methods of preventing premature cracking before titanium alloys became materials of choice for integrity critical structures in supersonic aircraft and others.

---

## 1.4 HT Materials

Various high-temperature materials are in use and an extensive review is given in Chapter 3. This chapter includes discussions related to some of the properties of concern to users of high-temperature materials. Generally, these properties include friction and wear, tensile strength, compressive strength, bearing strength, shock, electrical properties, thermal CTE, and heat capacity. Herein, a brief review is given to provide a broad background. When referring to composite materials the discussion covers materials that consist of two or more bonded constituents having significantly different physical or chemical properties. Composite materials consist of filler in the form of fibers or powder and a matrix of a monolithic material that is reinforced by the embedded filling component(s). Other high-temperature materials include refractory materials. These materials retain their strength at high temperatures and, according to ASTM C71, they have chemical and physical properties that make them applicable at temperatures above 538°C (1000°F).

### 1.4.1 Carbon–Carbon Composites

Carbon fiber-reinforced carbon, also known as carbon–carbon composites, is an effective high-temperature material for structural applications that require thermal shock resistance, a low coefficient of thermal expansion, thermal protection, lightweight, and good strength retention up to about 1400°C (Tenny et al., 1988). However, they have low impact resistance and, in the pure form of carbon–carbon composites, they are susceptible to significant oxidation at temperatures above about 500°C. To address the oxidation issue, overcoat sealers are used; however, in applications to high-speed flight vehicles, such overcoats are not an effective solution due to the fact that long duration of heat exposure can rapidly erode the coating if it is based on low viscosity sealants. Applying coating layers that consist of SiC and hafnium carbide (Ohlhorst et al., 2006) was determined to be effective in preventing oxidation at temperatures as high as 2200°C (Ohlhorst et al., 2006). Carbon–carbon composites are used for making structures of high-speed flight vehicles, such as the nose leading edge, horizontal control surfaces, and the tail leading edge (Ohlhorst et al., 2006). Other applications include aircraft brakes, high-temperature bearings and clutches, nozzles, exit cones, satellite structures, and heat shields. Also, for protection against the reentry temperature that exceeds 1260°C, the Space Shuttle nose cap (see Figure 1.3), its chin area between the nose cap and nosewheel doors, and the wing leading edges were also made of carbon–carbon.

### 1.4.2 Carbon–Silicon Carbide Ceramic Matrix Composite

Carbon fiber-reinforced silicon carbide has a relatively constant strength at temperatures up to 1600°C and the use of carbon fiber makes this composite material lightweight (Schmidt et al., 2004). It has a relatively low load-bearing properties resulting from micro-cracking that are produced during its fabrication and the formation of empty spaces that are micro-structural voids that are produced during the carbon fiber weaving (Glass et al., 2002).

### 1.4.3 Ceramics

Ceramics are inorganic nonmetallic solids that have mostly crystalline structures but, as in the case of glass, they may have amorphous structure. Certain ceramic materials, including silicon borides, carbides, and nitrides, can sustain extreme temperatures of more than



**FIGURE 1.3**

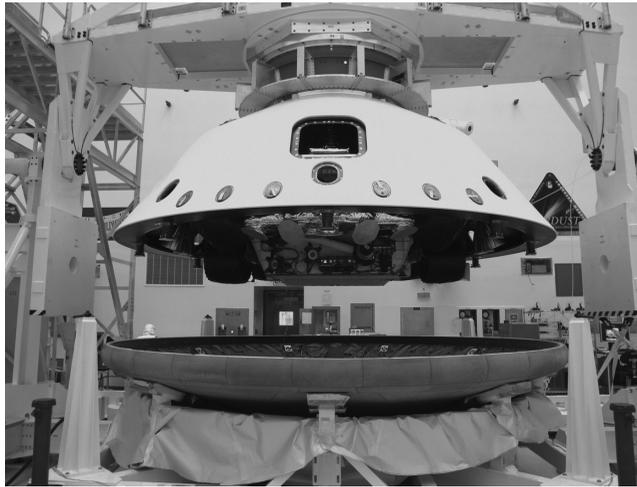
The nose cap of the Space Shuttle was made of carbon-carbon. (From Wikimedia Commons, [http://en.wikipedia.org/wiki/Space\\_Shuttle\\_thermal\\_protection\\_system#cite\\_note-tech-0](http://en.wikipedia.org/wiki/Space_Shuttle_thermal_protection_system#cite_note-tech-0); high resolution image: [http://upload.wikimedia.org/wikipedia/commons/2/2f/Thermal\\_protection\\_system\\_inspections\\_from\\_ISS\\_-\\_Shuttle\\_nose.jpg](http://upload.wikimedia.org/wikipedia/commons/2/2f/Thermal_protection_system_inspections_from_ISS_-_Shuttle_nose.jpg).)

2000°C (Wuchina et al., 2007). Ceramics are used for handling molten metals, and for aerospace applications such as hypersonic flight, scramjet propulsion, rocket propulsion, and thermal shield for atmospheric reentry. For these applications, the materials are used to produce nozzles of gas burners, nuclear fuel uranium oxide pellets, coatings of jet engine turbine blades, ceramic disk brakes, nose cones of missile, as well as refractory applications in furnaces of materials production. Also, they were used to produce the protection tiles of the Space Shuttle.

#### 1.4.4 Ceramic Composites

For thermal protection of structures, increasingly ceramic composites such as hafnium diboride and zirconium diboride are being used (Opeka et al., 2004). This is the result of their very high melting point of about 3200°C, high oxidation resistance up to 2000°C (Opeka et al., 2004), and their low ablation rates at high temperatures (Malone, 2000). One of the most effective ceramic composites that have been used in heat shields is the phenolic impregnated carbon ablator (PICA).

**PICA** is a lightweight ceramic ablator that is designed to burn away slowly and in a controlled manner. This is done in order to carry heat away from the spacecraft by the gases generated in the ablative process while the remaining solid material insulates the craft from superheated gases. PICA was developed in the 1990s at the NASA's Ames Research Center. It has a very low density (weighing about 20% of conventional heat shields), and can withstand temperatures as high as 1930°C. The material consists of carbon fibers coated with a thin layer of phenolic polymeric resin. While the resin provides bonding, it also creates a light, durable, and heat-resistant shield. In January 2006, PICA was used on the NASA's Stardust Sample Return Capsule (SRC) and it entered the Earth's atmosphere at the fastest recorded entry speed. Another well-known application of PICA for a heat shield was on the Mars Science Lab (MSL) that landed on Mars in August 2012 (see a photo of this heat shield in Figure 1.4). Due to the large size of the Curiosity Rover of the Mars Science Laboratory mission, a single-piece heat shield could not be used (Beck et al., 2010) and therefore a total



**FIGURE 1.4**

(See color insert.) PICA was used in tiles form to produce the heat shield (bottom cone) of the MSL mission that landed on Mars in Aug. 2012. (Courtesy of JPL/NASA, Reference Figure No. MSL-2011-05-26-143545-IMG\_0959.JPG.)

of 113 tiles (3.2 cm thick) were employed with adhesive that filled the gap between them. The produced heat shield was capable of sustaining thermal loading of  $197 \text{ W/cm}^2$ .

#### 1.4.5 Cermets

These are ceramic-metallic composites that combine the high-temperature resistance and hardness properties of ceramics with the ability of metals to deform plastically. The metal, which may be cobalt molybdenum or nickel with less than 20% in volume, serves as a binder of the ceramic constituent that may be a boride, carbide, or oxide. Other metallic constituents may be a nickel-based superalloy with such elements as columbium, molybdenum, and tantalum (Jenkins and Landis 2003) in a matrix of high-temperature ceramic material such as silicon carbide (SiC) (Jenkins and Landis, 2003). Cermets are used in high-temperature electronics to produce resistors and capacitors, as well as other components such as seals of fuel cells.

#### 1.4.6 Metal Matrix Composites

These materials consist of at least two constituents and with at least one made of metal, while the other one(s) can be a different metal, ceramic, or other material(s). These materials are also called hybrid composites when the MMC consists of three or more constituents. Generally, at elevated temperatures the creep and yield strengths of MMC are relatively higher compared to most metal alloys. Increasingly, MMC are used in high-performance systems and example includes a structural component of the landing gear F-16 Fighting Falcon jet aircraft. This component is made of monofilament silicon carbide fibers in a titanium matrix (a photo of the landing gear of the F-16 can be seen in Figure 1.5). An example of an effective MMC is the titanium MMC. It is capable of sustaining extensive cyclic loading in corrosive environments (Stephens, 1987) and structures made of this composite can endure temperatures as high as  $1650^\circ\text{C}$  (Stephens, 1987).



**FIGURE 1.5**

A structural component of the landing gear F-16 Fighting Falcon jet aircraft is made of metal matrix composite, [http://en.wikipedia.org/wiki/Metal\\_matrix\\_composite](http://en.wikipedia.org/wiki/Metal_matrix_composite). (From Wikimedia Commons, high resolution: [http://upload.wikimedia.org/wikipedia/commons/0/05/F-16\\_CJ\\_Fighting\\_Falcon.jpg](http://upload.wikimedia.org/wikipedia/commons/0/05/F-16_CJ_Fighting_Falcon.jpg))

Examples of titanium MMC include

**Titanium–Aluminum alloy:** This MMC is a high strength alloy with good air oxidation resistance for temperatures up to 650°C (Draper et al., 2007), where above 650°C it sustains oxidation and embrittlement (Tobin, 1997). This problem can be overcome by producing a stable oxide layer during the stage of fabrication. But, this process can also produce undesirable characteristics such as very low ductility, low fracture toughness and poor creep properties (Tobin, 1997). To prevent the oxidation, Ti–Al alloy substrates are suspended in vapor of aluminum to create a uniform coating layer of TiAl<sub>3</sub> (Draper et al., 2007).

**Titanium–Zirconium–Molybdenum alloy:** This alloy has high strength and, with a dispersion of TiC and ZrC in the molybdenum matrix, its high strength at elevated temperatures is well preserved. The carbide complexes (TiC and ZnC) provide benefit in making this composite highly weldable. Its low coefficient of thermal expansion allows designers to integrate this composite material at areas that are exposed to high temperatures without the need to prevent potential buckling from thermal stresses (Paull, 2006).

#### 1.4.7 Refractory Metals

These are metals that have extremely high melting points, have significant resistant to heat and wear, and they are very stable against creep deformation. The elements that are included in this category are molybdenum, niobium, rhenium, tantalum, and tungsten. These elements have melting point above 2000°C and they are very hard at room temperature. Applications of refractory metals include casting molds and wire filaments (see example in Figure 1.6) and they are widely used in powder metallurgy. There are also silicon-based refractory compounds, including SiC, Si<sub>3</sub>N<sub>4</sub>, and MoSi<sub>2</sub>,



**FIGURE 1.6**

The filament of a 200 Watt incandescent light bulb, [http://en.wikipedia.org/wiki/Refractory\\_metals](http://en.wikipedia.org/wiki/Refractory_metals). (From Wikipedia, <http://upload.wikimedia.org/wikipedia/commons/0/08/Filament.jpg>.)

which have excellent oxidation resistance at temperatures as high as 1700°C (Wuchina et al., 2007).

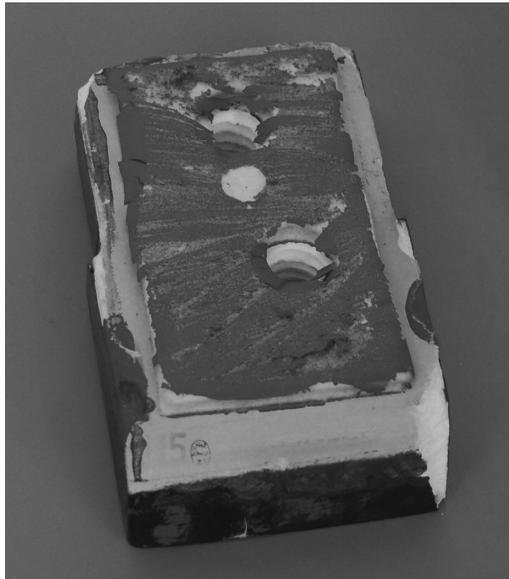
One of the widely used refractory materials is silica. The need for lightweight insulation and low heat conductivity has been addressed in the Space Shuttle thermal protection system by covering it with tiles made of Li-900. This material was developed and manufactured by Lockheed Missiles and Space Company in Sunnyvale, California. Li-900 consists of 10% in volume of silica fibers that are made of pure quartz and the rest is air and this combination leads to 0.144 g/cm<sup>3</sup> bulk density (Jenkins, 2007). Due to the fact that these tiles are not flexible, the Space Shuttle Orbiter (the orbital spacecraft of the Space Shuttles) was covered with thousands of tiles that were glued to its surface (see an example of a tile in Figure 1.7). The low impact resistance of the tiles on the Space Shuttle Orbiter was the cause of the Columbia destruction in 2003 during its return to Earth. This took place after piece of insulation foam fell from the external tank and impacted the tiles. The debris struck the leading edge of the left wing and damaged the Shuttle's thermal protection system that shields the vehicle from the intense heat generated from atmospheric compression during reentry ([http://www.nasa.gov/columbia/home/CAIB\\_Vol1.html](http://www.nasa.gov/columbia/home/CAIB_Vol1.html)).

### 1.4.8 Superalloys

Superalloys, also known as high-performance alloys, are materials with excellent mechanical strength and creep, good surface stability, and corrosion and oxidation resistance at high temperatures. The base elements of most superalloys consist of nickel, cobalt, or nickel-iron. Examples of superalloys include

**Hastelloy:** This group of superalloys consists of 22 different nickel-based, highly corrosion-resistant metal alloys. The name is a registered trademark name of Haynes International, Inc. Besides nickel, the following elements are used: molybdenum, chromium, cobalt, iron, copper, manganese, titanium, zirconium, aluminum, carbon, and tungsten. Hastelloys are applicable to corrosive and erosive environments and they are used in pressure vessels of chemical reactors, distillation equipment, nuclear reactors, as well as chemistry pipes and valves.

**Inconel:** This superalloy is based on nickel–chromium. Its strength gradually decreases as the temperature reaches about 650°C (Jenkins and Landis, 2003) and



**FIGURE 1.7**

A photo from the backside of one of the Space Shuttle tiles. (From Wikipedia, [http://en.wikipedia.org/wiki/File:Shuttle\\_tile.jpg](http://en.wikipedia.org/wiki/File:Shuttle_tile.jpg); high resolution image: [http://upload.wikimedia.org/wikipedia/commons/6/6f/Shuttle\\_tile.jpg](http://upload.wikimedia.org/wikipedia/commons/6/6f/Shuttle_tile.jpg).)

it is relative easy to create complex shapes with this superalloy. To avoid stress cracking in welded structures, which may result from thermal stresses, softer weld materials are used.

**Rene alloys:** This superalloy is also nickel-based and it maintains its room temperature strength to as high temperatures as 980°C (Smith, 2001; Hebel, 1963). These alloys are used to produce jet engine and missile components that require very high strength at high temperatures. The outer shell of the NASA Mercury capsule was made of Rene 41 alloy.

**Waspalloy** is an age hardened austenitic nickel-based superalloy that maintains excellent strength and good corrosion resistance up to about 980°C. The name of this alloy is a registered trademark of United Technologies Corp. and it is used for high-temperature applications such as gas turbines.

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## 1.5 HT Processes

Effective processing methods are critical to the availability of high-temperature materials for practical applications. Understanding the chemical kinetics, fluid dynamics, thermodynamics, and transport phenomena are essential to controlling and optimizing the processes of fabricating high-temperature materials. Besides the ability to produce such materials there is increasing need to address their environmental impact as well as the ability to recycle the produced materials. Furthermore, there are major developments in the area of processing of nano-scale materials and they are leading to important material capabilities.

Owing to the challenges that are involved with the processing and fabrication of high-temperature materials, there are many different methods that have emerged to address the needs of the specific materials and related properties. The higher the temperature that is applied in the processes, the greater the acceleration of the related kinetics and the reaction rate tends to be exponential with the temperature. Processing at high temperatures increases the solubility of various oxides when forming dissolutions, as well as enabling certain reactions and phase transformations that are essential to some of the produced materials. Rapid cooling is also used in some of the processes and it prevents molecules in the molten phase from rearranging into crystallographic structures. Thus, amorphous solids can be formed allowing the fabrication of metastable phases.

Some of the processing methods include smelting, powder sintering, and roasting, and they require sufficient understanding of the related kinematic and thermodynamic processes, effective process modeling, simulation, and optimization capabilities, as well as the ability to measure physical properties at high temperatures (Chapter 7). The processing methods include vacuum deposition methods, such as physical vapor deposition (PVD), where thin films are deposited by condensation of desired film material in vaporized form onto various part surfaces. This coating method involves high-temperature vacuum evaporation and condensation, or plasma sputter bombardment. Another deposition process is the chemical vapor deposition (CVD), which is a chemical process that is used to produce high-purity, high-performance solid materials. Generally, the modeling of processes involves both theoretical and experimental studies and includes multi-phase equilibrium modeling to allow predicting reaction equilibrium and transport properties of complex multicomponent and multiphase systems. The models involve using computational fluid dynamics (CFD) that are also used to simulate fluid flow in high-temperature systems. The performance of high-temperature metallurgical systems can be affected by a number of factors including: liquid and solid chemistries; reaction kinetics; such physical properties as viscosity and surface tension; transport properties including electrical and thermal conductivity; interfacial properties between liquids, solids, and gases. Some of the properties that need to be measured include the viscosity, as well as the surface and interfacial tension at high temperatures, electrical properties, thermal conductivity, and the reaction rates and order.

Increasingly, producers of high-temperature materials need to reduce greenhouse gas emissions, improve product quality and productivity, and improve the energy efficiency of the production processes.

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## 1.6 Actuators, Devices, Mechanisms, and Jet Engine Turbines

Making devices, mechanisms, and actuators that can operate at high temperatures is a great challenge and it increases as the temperature is raised (Chapters 9 through 17). The related issues that need attention include material compatibility, chemical reactions, alloying, annealing, and diffusion characteristics. These may affect the chemical and physical nature of the components that are used. One of the key mechanical design issues is a mismatch of the thermal expansion coefficients, and this can be catastrophic to components that need to fit precisely inside a structure.

Driving mechanisms at high temperatures requires adequate capability of the actuators and their drive and control electronics. Due to technology limitations, most electronic

devices are limited to the maximum range of 250–300°C, whereas the actuators that are driven by coils or electroactive materials are limited to applications in the range of up to about 500°C (Chapters 9 through 12 and 17; Bar-Cohen and Zacny, 2009).

Turbojet engines are operated at much higher temperatures and the specific temperature is bounded by the durability of the blades and the nozzle materials (Stone, 1999). The combustion chamber of these engines burns fuel at large quantities and it is supplied via spray nozzles. The work, which is done by the compressor, raises the air temperature to the range of 200–550°C, while the combustion process raises the temperatures to the range of 650–1150°C. After combustion, the gas temperature reaches the range of about 1800–2000°C, which may be too high for the turbine nozzle guide vanes. To lower the temperature inside the combustion chamber, the emitted gas is used for cooling.

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## **1.7 NDE and Characterization Methods for HT Materials and Mechanism**

A critical part of assuring the ability of high-temperature materials to sustain the operating conditions for which they are designed is their integrity, material quality, and the properties consistency with the design requirements (Bar-Cohen et al., 2003; Chapter 8). The detection of defect and the characterization of properties without affecting the integrity of the material or structure require the use of nondestructive testing (NDT) or nondestructive evaluation (NDE) methods. Increasingly, in-service nondestructive health monitoring methods are used to monitor the integrity of structures and materials properties. The term health monitoring is inspired by the medical term of monitoring the health of our body and similarly it is essential to monitor and control the material integrity and properties at all stages of the structure's life, from cradle to retirement. A typical health monitoring system consists of a sensor, data acquisition, and setup for processing and controlling the system using a microprocessor that acquires and analyzes the data, providing real-time information. The methods that are used at room temperature to inspect high-temperature materials include the common ones such as ultrasonics, magnetic-particles, liquid penetrants, radiography, thermography, visual inspection, eddy-current testing, and laser interferometry. While most NDE methods are applied at room temperatures, certain methods of health monitoring of high-temperature materials and mechanisms can be applied at the elevated temperatures, which may reach several hundreds of degree Celsius. Besides the use of NDE methods, characterization methods are used to examine the materials, structures, and mechanisms at room temperatures. These methods are also used to test representative samples of actual parts and structures that are subjected to service conditions and tested afterward at room temperature (Chapter 7). These methods are used to perform surface, bulk, and structural analysis using various tools that include chemical and mechanical analysis.

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## **1.8 Summary/Conclusions**

Development of high-temperature materials that can maintain their properties and integrity are critical to applications where extended exposure to hot conditions is required. Generally,

even primitives used such materials in the earlier days of civilization but, with time, materials and processes were developed to allow more control over the properties of the produced materials leading to commercial quantities. Despite the significant efforts, the materials that need to operate at extreme temperature environments possess certain related limitations. These require engineering their applications to work within their acceptable limits.

Many advances in developing high-temperature materials have been made in the past 50 years, particularly for such applications as high-speed flight vehicles such as the Space Shuttle and hypersonic vehicles. Generally, the required materials need to be lightweight, have high tolerance to cyclical loading, and the ability to form into complex shapes. High heating rates and temperatures that are reached during service pose many engineering challenges that led to the development of many effective materials, as well as methods of thermal management. The developed materials include high-temperature metal alloys, superalloys, MMC, ceramic composites, and carbon-carbon composites. Key factors in choosing materials for high-temperature applications include the cost and the complexity of fabrication. To support the capability of high-temperature materials to endure the related harsh conditions effective coating methods are applied to prevent oxidation and surface cracking.

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- Meetham G.W., and M.H. Van de Voorde, *Materials for High Temperature Engineering Applications*, Section 1.2 “High Temperature Materials” at Google Books: [http://books.google.com/books?id=cx11I9lVLcC&pg=PA3&source=gbs\\_toc\\_r&cad=4#v=onepage&q&f=false](http://books.google.com/books?id=cx11I9lVLcC&pg=PA3&source=gbs_toc_r&cad=4#v=onepage&q&f=false)
- MSL—Aeroshell and Heat Shield, viewed on August 10, 2012, <http://www.spaceflight101.com/msl-aeroshell-and-heat-shield.html>

- Principles of Jet Engine Operation, viewed on August 10, 2012, <http://www.century-of-flight.net/Aviation%20history/evolution%20of%20technology/jet%20engines.htm>
- Refractory Metals: Niobium, Molybdenum and Rhenium, viewed on August 05, 2012, <http://www.key-to-metals.com/Article123.htm>
- Report of Columbia Accident Investigation Board [http://www.nasa.gov/columbia/home/CAIB\\_Vol1.html](http://www.nasa.gov/columbia/home/CAIB_Vol1.html)
- Thermographic nondestructive evaluation of the space shuttle main engine nozzle, viewed on August 10, 2012, [http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20000096499\\_2000138014.pdf](http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20000096499_2000138014.pdf)
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# 2

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## *High-Temperature Materials Chemistry and Thermodynamics*

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Sulata Kumari Sahu and Alexandra Navrotsky

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### 2.1 Introduction

Many of the uses of materials at high temperature require their persistence, with minimal change in chemical composition and microstructure, over long periods of time (hours to years). Chemical reactions at high temperature often occur fast and thus the thermodynamic equilibrium state, rather than persistence of metastable states, often governs the suitability of a given material or set of materials for a proposed application. The term “high temperature” cannot be defined uniquely; perhaps the most useful practical definition is one that says that for a given material, high temperature is the temperature above which the material is strongly chemically reactive in use. From the point of view of solid state chemistry and thermodynamics, there is vast empirical knowledge about such reactivity and moderately adequate thermodynamic data bases for common alloys and ceramics (Sundman et al., 1985; Schenck and Dennis, 1989; Pankratz, 1982; Ondik and Messina, 1989; Liu et al., 2003; Levin and McMurdie, 1975; Kubaschewski and Alcock, 1979; Gisby et al., 2002; Eriksson and Hack, 1984; Davies et al., 2002; Chase et al., 1985a,b; Chart, 1978; Barry et al., 1979). Nevertheless, an inexperienced or only moderately knowledgeable scientist or

engineer may have a hard time selecting materials for high temperature use and avoiding pitfalls of unanticipated reactivity and degradation. The purpose of this article is to organize such chemical knowledge into a short and useful guide on materials use and compatibility, taking advantage of general trends governed by the regularity of chemical bonding and thermodynamics among groups of elements in the periodic table.

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## **2.2 How Materials Fail at High Temperature**

This section briefly summarizes failure modes (Walter, 1999; Tillack, 2000; Priest, 1992; Kerans, 2000; Jarvis, 2006; Danzer, 1993; Blachnio, 2009; Johnson, 1950; Ashby and Jones, 2005). More than one process can occur simultaneously. The following sections give specific examples and general trends.

### **2.2.1 Melting and Softening**

Obviously melting destroys the integrity of a solid and the melt or partial melt (melt/crystal “mush”) is generally chemically very reactive with its environment. Thus, one needs high melting compounds for high-temperature applications. Impurities usually lower the melting point, and deep eutectics can be disastrous. Glasses do not melt but they soften on going through their glass transition. Glasses can crystallize, sometimes transforming a dense solid material to a porous powdery one. Even crystalline solids become soft and deformable at high temperature and brittle materials become ductile (Petty et al., 1968). Such effects occur typically above about two-thirds of the melting point in degrees Kelvin.

### **2.2.2 Vaporization**

Many solids vaporize (sublime) rather than melt. Others melt and then boil. At reduced pressure vaporization is more extensive. The vaporization behavior of metals and their oxides can be quite different (Tietz and Wilson, 1965). For example, metals such as tungsten, molybdenum, rhenium, and osmium are refractory and useable to temperatures above 2000°C, while their oxides are low melting and volatile. Their ready oxidation and the poor high-temperature behavior of their oxides limit the use of such metals to non-oxidizing environments (inert gas or vacuum).

### **2.2.3 Corrosion and Chemical Reaction with the Atmosphere**

Reactions include oxidation, nitridation, reaction with H<sub>2</sub>O and CO<sub>2</sub> to form hydrates and carbonates, and reaction with traces of HCl, SO<sub>2</sub>, and other corrosive gases. Oxidation, especially of small particles and dusts, can be explosive and reaction of active metals such as zirconium with water to form the metal oxide plus hydrogen can lead to hydrogen explosions if air is also present. Such hydrogen explosions, with H<sub>2</sub> generated by the reaction of zirconium-containing fuel rod cladding (zircalloy) with water or steam (Grosse et al., 2010; Kim et al., 2010; Tanabe, 2011) are the major source of breach of containment in nuclear reactor accidents such as those at Chernobyl and Fukushima (Armstrong et al., 2012; Burns et al., 2012). One should also note that nitrogen is not always a suitably inert

gas for metals that readily form stable nitrides at high temperature, for example, titanium, zirconium, and tantalum (Loremez and Woolcock, 1928; Gulbransen and Andrew, 1950; Ono et al., 1996; Fromm, 1970; Wilkinson, 1969).

#### 2.2.4 Diffusion and Solid-State Reaction

When two different materials are in contact, they will diffuse into each other or form a layer of reacted material if such reaction is thermodynamically favorable. Grains will grow and the material may become porous and change in other physical properties. In composite structures, such as thermal barrier coatings, different layers may delaminate or material may spall off. On the other hand, adherent protective coatings of reacted (oxidized) metal or intentionally added other protective layers can greatly extend the use and lifetime of materials at high temperature, for example, in protective oxide layers and thermal barrier coatings (Stowell et al., 2001; Schmitz and Stamm, 2009; Igolkin, 2003; Beele, 1999).

#### 2.2.5 Solid–Solid Phase Transformations

If there are phase transitions among different crystal structures, the properties of the high-temperature phase may be quite different from those of the low-temperature phase (Lopato et al., 1974; Navrotsky and Ushakov, 2005; Wang et al., 1992; Eyring, 1979; Adachi and Imanaka, 1998; Barnal et al., 2004). If the phase transition involves a large volume change, cracking or disintegration may occur (Navrotsky and Ushakov, 2005; Wang et al., 1992; Scott, 1975).

Various elements, alloys, and oxides are used in high-temperature applications as structural elements, resistive heaters, and containers. Table 2.1 lists the more common ones and their approximate upper temperature for continuous use in a given atmosphere and common mode of failure. The reader is warned that there is no such thing as a totally inert material at temperatures above about 1500°C, and often one has to choose the least deleterious scenario rather than the perfect solution for a given application.

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### 2.3 Noble Metals

Platinum and platinum–rhodium alloys are used for thermocouples, electrodes, and sample crucibles at high temperature (Rajan, 2004; Pollock, 1985; Swindells, 1968; Groza et al., 2007; Soszko et al., 2011). Rhodium raises operating temperature and adds strength (Ochiai, 1993; Winkler, 2000). Iridium is also sometimes used for crucible material; it is higher melting and strong but even more expensive than platinum (Cardarelli, 2000). Common thermocouple types, with wires commercially available, are given in Table 2.2, which also gives data on use temperatures and melting points of various noble metals. Though platinum group metals are considered to be noble metals, they in fact chemically reactive under a variety of conditions, sometimes with disastrous consequences to the user. There are a number of binary and ternary noble metal oxides (see Table 2.3), whose stability is generally limited to temperatures below about 1150°C (Jehn, 1984; Krier and Jaffe, 1963; Raub, 1959; Raub and Plate, 1957; Schwartz and Prewitt, 1984; Jacob et al., 2009; Chaston, 1964, 1969, Bettahar et al., 1987; Tancret et al., 1996) and is of course enhanced by strongly oxidizing conditions such as a pure oxygen atmosphere. Platinum

TABLE 2.1

Various Elements, Alloys, and Oxides Used in High Temperature Applications

Materials	Approximate Upper Use Temperature (°C)	Atmosphere	Common Mode of Failure
Nickel–chromium–iron alloys (American Foundrymen's Association, 1957; Taylor, 1991; Hussain et al., 1995)	900–1100	Various	a, b, c
Iron–chromium–aluminum alloys (Prescott and Graham, 1992)	1000–1150	Various	a, b, c
Ti–Ni–Al alloys (superalloys) (Wang et al., 1995)	800–1000	Various	a, b, c
Molybdenum	<500 1600	Oxidizing Reducing	a, b, c, d
Platinum (Jahn, 1984)	1600	Various	b, c, d
Iridium (Cardarelli, 2000)	2200	Various	b, c, d
Rhodium (Jahn, 1984)	1700	Oxidizing Reducing Vacuum	
Tantalum (Wilkinson, 1969)	1000 800 2200	Oxidizing Nitrogen Reducing	a, b, c, d, g
Tungsten (Wilkinson, 1969)	<500 2200	Oxidizing Reducing	a, b, c, d
SiC (Singhal, 1976)	1700	Reducing	a, c, d
Si <sub>3</sub> N <sub>4</sub> (Singhal, 1976)	1400	Reducing	a, c, d
C (graphite) (Jahson, 1950)	2000	Reducing	a, c, d
MoSi <sub>2</sub>	1700 1350	Oxidizing, forms a protective coating Reducing	
ThO <sub>2</sub> (Jahson, 1950)	2300	Oxidizing, reducing	b, e
MgO (Jahson, 1950)	1600–1700	Oxidizing, reducing	b, d, e
ZrO <sub>2</sub> (Jahson, 1950; Cardarelli, 2000)	2300	Oxidizing	b, e, f
Al <sub>2</sub> O <sub>3</sub> (Jahson, 1950; Cardarelli, 2000; Badkar, 1991)	1950	Oxidizing, reducing	b, e, f

Source: Geddes, B. et al., *Superalloys: Alloying and Performance*, ASM International, SBN: 9781615030408, 2010, pp. 1–176; Davis, J. R. *ASM Specialty Handbook: Heat-Resistant Materials*, ASM International. ISBN: 0871705966, 1997, pp. 1–591, 51.

<sup>a</sup> Oxidation.

<sup>b</sup> Grain growth.

<sup>c</sup> Temperature lowered if corrosive gases or various incompatible metals oxides are present.

<sup>d</sup> Vaporization.

<sup>e</sup> Melting.

<sup>f</sup> Phase transformation a problem, “stabilized zirconia avoids this but may have somewhat lower temperature limit.

<sup>g</sup> Forms nitrides.

TABLE 2.2

Properties of Standard Thermocouples

Type	Base Composition	Melting Point (°C)	Ambient	Temperature Range (°C)
J	Fe (+)	1400	Oxidizing or reducing	7–600 <sup>a</sup>
	44Ni-55Cu(-)	1210		
K	90Ni-9Cr(+)	1350	Oxidizing	-270–1372 <sup>a</sup>
	94Ni-Al,Mn, Si, Fe, Co(-)	1400		
N	84Ni-14Cr-1.4Si(+)	1410	Oxidizing	-270–1260 <sup>a</sup>
	95Ni—4.4Si-0.15 Mg(-)	1400		
T	Cu(+)	1083	Oxidizing	-200–370 <sup>a</sup>
	44Ni-55Cu(-)	1210		
E	90Ni-9Cr(+)	1350	Oxidizing	-200–870 <sup>a</sup>
	44Ni-55Cu(-)	1210		
R	87Pt-13Rh(+)	1860	Oxidizing or inert	-50–1768
	Pt(-)	1769		
S	90Pt-10Rh(+)	1769	Oxidizing or inert	-50–1768
	Pt(-)	1927		
B	70Pt-30Rh(+)	1927	Oxidizing, vacuum, or inert	800–1820
	94Pt-6Rh(-)	1826		
C	W-5Re (+)	3350	Inert	0–2760 <sup>a</sup>
	W-26Re (-)	3120		

Source: Davis, J. R. *ASM Specialty Handbook: Heat-Resistant Materials*, ASM International. ISBN: 0871705966, 1997, pp. 1–591–51. From Springer Science+Business Media: *Materials Handbook: A Concise Desktop Reference*, 1st Edition, 2000, pp. 1–595, Cardarelli, F.

<sup>a</sup> Use in oxidizing atmospheres limited by easy oxidation of the metals, may be used somewhat higher in inert atmospheres, but wires become very brittle on heating.

is also seriously corroded by basic oxides such as Na<sub>2</sub>O and K<sub>2</sub>O, especially when these melt. Under reducing conditions, one must be cautious when using platinum because of its tendency to react with base metals, often to the extent of pulling them out of oxides in contact with it (Berndt and Keller, 1974). Lead precipitated in the grain boundaries of platinum appears to enhance grain growth and can weaken grain—grain contacts and

TABLE 2.3

Binary and Ternary Platinum Oxides

Oxide	Decomposition Temperature (°C)
PtO	555
OsO <sub>4</sub>	Boils at 130
IrO <sub>2</sub>	1100
RhO <sub>2</sub>	1127
RhO	1120
Rh <sub>2</sub> O <sub>3</sub>	880
PtO <sub>2</sub>	430
Pb <sub>2</sub> PtO <sub>4</sub>	735
PbPt <sub>2</sub> O <sub>4</sub>	750
Ca <sub>2</sub> Pt <sub>5</sub> O <sub>8</sub>	720

cause leaks in crucibles (Cardarelli, 2000; Darling et al., 1970a). Similarly, hot Pt should never be placed in contact with graphite. Iron and other transition metals will alloy with platinum, embrittle it, and change the composition of oxide samples contained in Pt foil or crucibles. At high temperatures, platinum will react strongly with refractories such as alumina, zirconia, and thoria when oxygen is effectively removed from the surrounding atmosphere. Magnesia is the only refractory so far examined which resists this type of decomposition, which can occur at temperatures as low as 1200°C (Darling et al., 1970a). There are very stable Pt-Zr intermetallic compounds, so Pt in contact with zirconia under reducing conditions can spell trouble (Darling et al., 1970a). Such reactions contaminating Pt thermocouples will change their e.m.f. (often decreasing it) and could cause erroneous apparently low-temperature readings which will be compensated by control systems and cause the furnace to overheat, sometimes to the point of melting the Pt. A low eutectic in the Pt-Si system is also a potential hazard. The binary phase diagrams for Pt-Si, Pt-Pb, Pt-Zr, Pt-Al (McAlister and Kahan, 1986) are given in Figure 2.1a through d. Table 2.4 shows the eutectics between low melting point metals and noble metals (Groza et al., 2007).

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## 2.4 Materials above 2000°C

In the absence of oxygen, tungsten, tantalum, and iridium can be used to temperatures of above 2000°C, encountering neither melting nor serious vaporization (Davis, 1997; Cardarelli, 2000). They can be used in vacuum or in an inert noble gas atmosphere but not in nitrogen because of potential nitride formation (Stowell et al., 2001; Schwarzkopf and Kieffer, 1953; Jehn and Ettmayer, 1978). They are used for containers, thermocouples (e.g. W-Rh) and heating elements (Wilkinson, 1969; Davis, 1997; Cardarelli, 2000; Schwarzkopf and Kieffer, 1953). However these metals oxidize easily, and their oxides, in contrast, melt and boil in the 800–1000°C range (Revie, 2010; Kofstad, 1966; Gulbransen and Wysong, 1948; Gulbransen et al., 1963). Thus, air or oxygen leaks in systems using these materials can cause catastrophic failure. Graphite can be used to about 2200°C (Johnson, 1950; Davis, 1997). It appears to sublime rather than melt, and has significant vapor pressure and mobility (as well as transport as CO gas species) above 2000°C (Palmer, 1970; Joseph et al., 2002; Scheindlin, 1984; Brewer, 1952). Thus, it is almost impossible to avoid carbon contamination of samples in graphite containers and furnaces, or even in high vacuum systems containing traces of carbon from lubricants or other sources. The formation of carbides of zirconium, titanium, tungsten, and molybdenum is a complication when these metals and graphite are present in the same high temperature system (Marmer et al., 1971).

Maintaining oxidizing conditions and a good sample containment/measurement environment above 2000°C is challenging because of the lack of appropriate materials. Table 2.1 shows few oxides with melting points above 2000°C, which in principle make suitable crucible materials or protective coatings. However, they themselves are reactive toward other oxides, often resulting in compounds with lower melting points or systems with deep eutectics (Jarvis, 2006; Danzer, 1993; Adachi and Imanaka, 1998; Davis, 1997; Cardarelli, 2000; Marmer et al., 1971). Dense thoria is an excellent crucible material, stable with no change in composition or structure in atmospheres ranging from air down to very low oxygen fugacity. It is slow to react with other oxides. Its use has gone out of vogue because of its modest radioactivity, but it remains very useful as a container, refractory, and when



**TABLE 2.4**

Noble Metal Eutectics (°C) with Selected Elements

Element	Pt	Rh	Ir
B	825	1131	1046
P	588	1254	1262
Si	890	1389	1470
Sn	1070	–	–
Pb	327	–	–
Bi	730	–	–
Sb	633	–	–
As	597	–	–

doped with rare earths, a solid electrolyte which maintains purely ionic conductivity down to extremely low oxygen fugacity (Chaudhary et al., 1980; Subbarao, 1980; Bonnell and Hastie, 1990; Fauquier, 1961). A number of oxides, notably the rare earth oxides, zirconia, and hafnia, undergo a series of phase transitions with substantial changes in enthalpy and volume, prior to melting, which can compromise their physical integrity (Navrotsky and Ushakov, 2005; Wang et al., 1992; Adachi and Imanaka, 1998; Navrotsky, 1994; Suresh et al., 2003; Pitcher and Navrotsky, 2003; Pitcher et al., 2005; Ushakov et al., 2004). Transition points and thermodynamic properties are listed in Table 2.5. A further complication is the existence of deep eutectics in oxide systems; which means that, although specific compounds may be stable to high temperature, melting can ensue as much as 500°C lower in binary and multicomponent systems (Bowen, 1914; Alper et al., 1962; Chatterjee and

**TABLE 2.5**

Phase Transitions and Thermodynamic Properties of Some Refractory Oxides

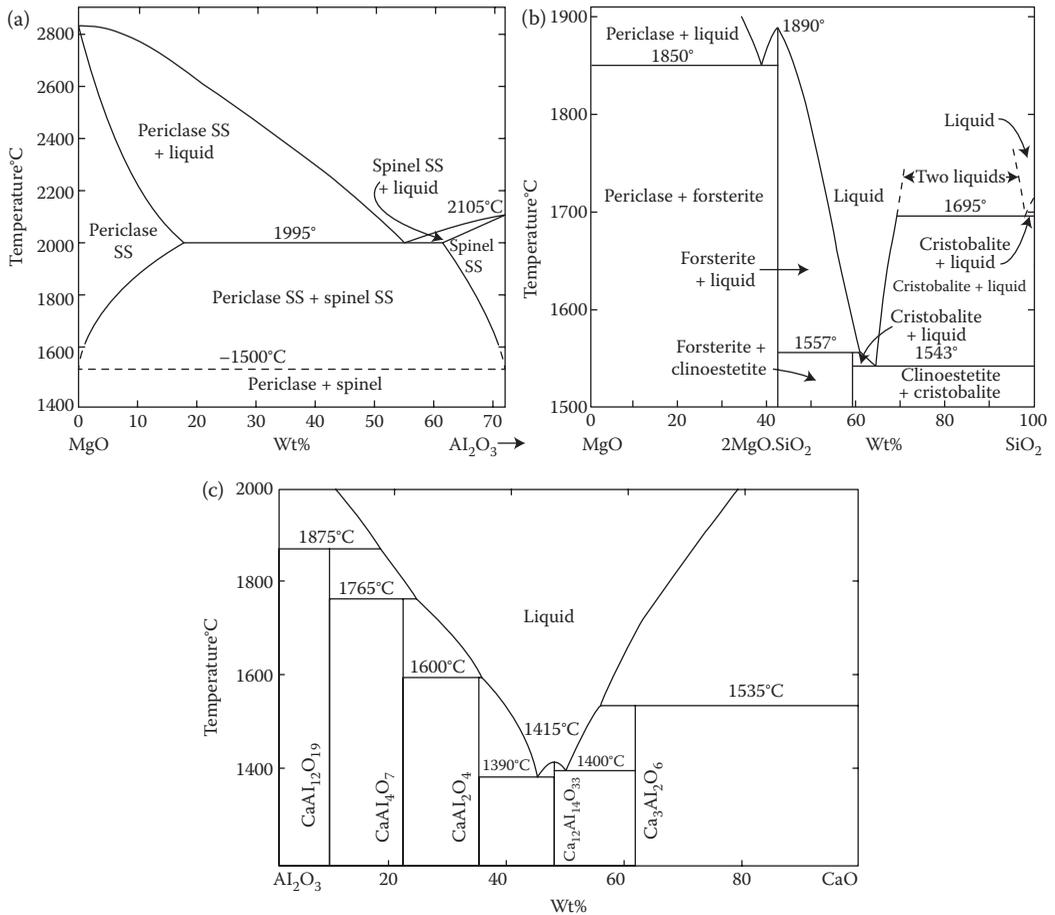
Oxide	Phase Transition	Transition Temperature (°C)	Enthalpy of Transition kJ.mole <sup>-1</sup>	Entropy of Transition J mol <sup>-1</sup> K <sup>-1</sup>
ZrO <sub>2</sub>	m-t	1202	5.4 ± 0.3	3.7 ± 0.3
	t-c	2300	4.2 ± 0.5	1.6 ± 0.2
	m-c	Metastable	9.6	5.3
HfO <sub>2</sub>	m-t	1650	32.5 ± 1.7	
	t-c	2700		
	m-c	Metastable		
Y <sub>2</sub> O <sub>3</sub>	C-c	2200 ± 50	24 ± 5	
SiO <sub>2</sub> (Stevens et al., 1997; Roy and Roy, 1964; Richet et al., 1982; Navrotsky et al., 1980)	Quartz-	870	1.32	
	tridymite	1473 ± 30	0.96 ± 0.25	
	tridymite-cristobalite	525	9.49 ± 0.25	
	cristobalite	835	10.20 ± 0.33	
	α-β	1427		
	cristobalite-quartz	1726		
	amorphous SiO <sub>2</sub> -quartz amorphous SiO <sub>2</sub> -cristobalite			

Source: Navrotsky, A., *Journal of Materials Chemistry*, 15(19), 2005, 1883–1890.

Note: M, monoclinic; t, tetragonal; c, cubic fluorite; C, cubic C-type (ordered vacancy).

Zhmoidin, 1972). Such effects are illustrated in the phase diagrams for MgO-Al<sub>2</sub>O<sub>3</sub>, MgO-SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>-CaO in Figures 2.2a, b, and c, respectively.

Considering a variety of compositions and composite materials can enhance design capability and functionality. Among the rare-earth chromite refractories, lanthanum chromite is the most refractory (m.p. 2487°C). It is also the least expensive and is under consideration as a high-temperature material for magnetohydrodynamic power generation (MHD). However, the limitation to the use of lanthanum chromite at very high temperatures is its volatility in oxidizing atmospheres due to volatilization of gaseous CrO<sub>3</sub>. Doping of lanthanum chromite with strontium reduces the volatility and improves the sinterability and conductivity (Khattak and Cox, 1977; Barnal et al., 2004; Wang et al., 2007; Setz et al., 2011; Acchar et al., 2012). Similarly when mullite impurity is added to the refractory material zircon (ZrSiO<sub>4</sub>), it improves sintering, making the production of high-density ceramics from zircon–mullite mixtures more efficient than than from pure zircon (Rendtorff et al., 2009, 2010; Yeo et al., 2004). Also the emissive properties of rare earth hexaborides (e.g.,



**FIGURE 2.2** (a) MgO-Al<sub>2</sub>O<sub>3</sub> phase diagram (Alper, 1962); (b) MgO-SiO<sub>2</sub> phase diagram (From Bowen, N. L. and O. Andersen, *American Journal of Science*, 37, 1914, 487–500.); (c) phase diagram Al<sub>2</sub>O<sub>3</sub>-CaO (From Chatterjee, A. K. and G. I. Zhmoidin, *Journal of Material Science*, 7(1), 1972, 93–97).

LaB<sub>6</sub>) improve by addition of refractory metals (tungsten, rhenium, titanium, and iridium) (Latini et al., 2002; Kondrashov, 1974; Bondarenko et al., 1971; Chu and Goebel, 2012).

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## 2.5 Silicon-Based Refractories

Silicon nitride and silicon carbide are excellent structural and refractory materials under neutral atmospheres up to 1400°C and 1700°C, respectively. Si<sub>3</sub>N<sub>4</sub> exists in two polymorphs,  $\alpha$  and  $\beta$ , the latter stabilized by oxygen impurities (Liang et al., 1999; Jansen et al., 2002; Chen, 1993). SiC shows many complex polytypes. Rare earth oxides are used as sintering aids for Si<sub>3</sub>N<sub>4</sub> and details of the mechanism of sintering and the nature and thermodynamics of intergranular crystalline, amorphous, and molten phases resulting from the interaction of nitride and oxide are still under study (Ashton, 2011; Nagano et al., 2000; Negita, 1986; Shui et al., 2011). In the past decade, the controlled pyrolysis of polymers with a silicon backbone and pendant organic groups has produced a new class of “polymer derived ceramics” (PDC) in the Si-O-C, Si-C-N, and Si-B-C-N systems (Tavakoli et al., 2012; Varga et al., 2007; Ionescu, 2012; Morcos et al., 2008a; Riedel et al., 1995, 2006; Seifert et al., 2001). Though amorphous to X-ray diffraction, they are heterogeneous at the nanoscale, with carbon rich and carbon poor (oxygen or nitrogen rich) domains. They withstand high temperature as well as or better than silicon nitride, though they are subject to crystallization, oxidation, and carbothermal reduction above 1500–1550°C. Thermochemical studies suggest considerable thermodynamic stability of PDCs relative to crystalline SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiC, and C (Morcos et al., 2008a,b; Seifert et al., 2001; Durham et al., 1991).

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## 2.6 High-Temperature Oxidation

Oxidation is an important high-temperature corrosion phenomenon, especially in metals and alloys. The rate of oxidation of metals usually decreases as oxide layer thickness increases. Very small amounts of reactive elements added to the alloy sometimes introduce a remarkable improvement in the integrity of the protective oxide, particularly in its resistance to thermal cycling (Sequeira, 2011a,b; Wright and Dooley, 2010; Boinovich et al., 2011; Del et al., 2012). The reaction product, a scale formed on the metal, acts as a physical barrier and, in favorable cases, reaction ceases after the barrier is established (Boinovich et al., 2011; Aiello et al., 2004; Fazio et al., 2001; Hata and Takahashi, 2006; Kurata and Futakawa, 2004; Zhang et al., 2005).

Thermodynamics provides an essential tool in the analysis of oxidation problems. Although not predictive of kinetics, thermodynamic analysis allows one to ascertain which reaction products are possible. It is useful to represent thermodynamic analysis in graphical form. The types of thermodynamic diagrams most often used are

1. Gibbs free energy versus composition diagrams, which are used for thermodynamics of solutions (gas, liquid, or solid) (Gaskell, 2003; Darken et al., 1953; Alper, 1970).

2. Standard Gibbs free energy of formation versus temperature diagrams, often called Ellingham diagrams, which show the thermodynamics for a given class of compounds, for example, oxides, carbides, nitrides, and sulfides (Ellingham, 1944). They allow immediate comparison of the relative stability of different materials, including solids with different oxidation states for the same metal (Ellingham, 1944; Shatynski, 1977, 1979; Olette and Ancey-Moret, 1963; Richardson and Jeffes, 1948; Kellogg, 1966; Belton and Worrell, 1970).
3. Vapor species diagrams, sometimes called Kellogg diagrams, which present the vapor pressure of compounds as a function of convenient variables such as partial pressure of gaseous components (Revie, 2010; Kellogg, 1966; Belton and Worrell, 1970).

The Ellingham diagram is a graphical representation of the standard Gibbs free energies of oxidation of pure metals vs. temperature (Gaskell, 2003). The most useful form of representation is to express the quantities in terms of one mole of the oxidizing species:



At a given temperature,  $T$ , the standard free energy  $\Delta G_T^0$  of the reaction is

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta G_T^0 \quad (2.2)$$

At equilibrium

$$\Delta G_T^0 = -RT \ln \left( \frac{a_{M_xO_2}}{a_M} \cdot f_{O_2}^{-1} \right) \quad (2.3)$$

where “ $a$ ” stands for activity and “ $f$ ” for fugacity. The stoichiometric coefficient  $x$  is 2 for an oxide  $MO$ , 1.5 for  $M_2O_3$ , and 1 for  $MO_2$ . If the metal oxide is stoichiometric, the gas is ideal, and there is negligible solubility of oxygen in the metallic phase, the activities of  $M$  and  $M_xO_2$  can be taken as unity and pressure can be substituted for fugacity. Thus,

$$\Delta G_T^0 = RT \ln p_{O_2} \quad (2.4)$$

Figure 2.3 is an Ellingham plot for binary oxides. The  $\Delta G_T^0$  values fall on a straight line in the diagram. The change in the slope of the line corresponds to the phase change of the metal or compounds. The partial pressure at which the metal and oxide coexist is the dissociation pressure of the oxide.

The relative stability of the various oxides is easily deduced from Figure 2.3. The most stable oxide have the most negative value of  $\Delta G_T^0$  the lowest value of  $P_{O_2}$  and the highest value of  $(P_{H_2}/P_{H_2O})$  and  $(P_{CO}/P_{CO_2})$ . Figure 2.3 shows clearly that oxides such as  $CaO$  and  $Al_2O_3$  can be reduced only under very low oxygen fugacity, and conversely, their metals are predicted to oxidize under a wide range of  $P_{O_2}$  conditions. The role of kinetics and protective coatings is demonstrated by the very different actual behavior of aluminum and calcium at ambient conditions. Aluminum generally forms a protective adherent alumina film and persists (metastably) for years under most conditions. Calcium oxidizes rapidly (potentially explosively) to  $CaO$  which in turn reacts with  $H_2O$  and  $CO_2$  in the atmosphere to form  $Ca(OH)_2$  and  $CaCO_3$ .

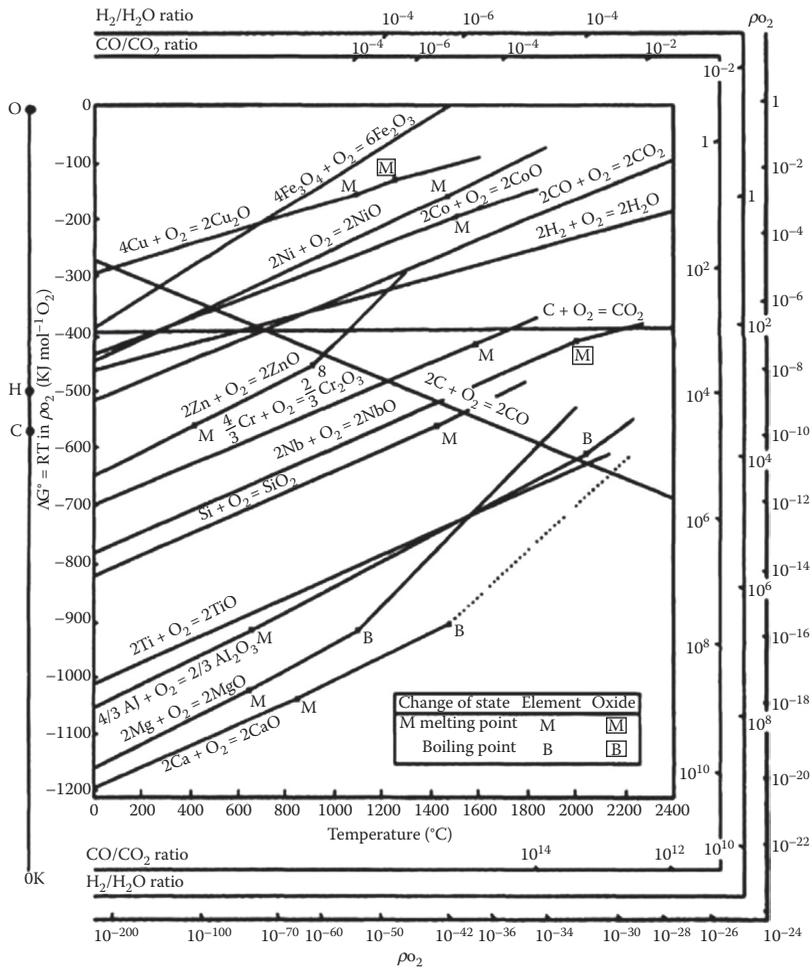


FIGURE 2.3

Ellingham plot for some common metal–metal oxides. (From Birks, N., G. H. Meier, and F. S. Pettit, *Introduction to the High Temperature Oxidation of Metals*, 2nd ed., Cambridge University Press, ISBN:9780521480420, 2006, 1–352.)

From Figure 2.3, it is clear that the oxides of Fe, Ni, and Co, which form the base of the majority of engineering alloys, are significantly less stable than the oxides of some solutes like Cr, Al, and Si. When one of these solute elements is added to Fe, Ni, Co, or their alloys, internal oxidation of the solute (the oxide remaining within the alloy as small particles) is expected to occur, if the concentration of the solute is relatively low. As the concentration of the solute increases, oxidation will change to external, resulting in an oxide scale that protects the alloy from rapid oxidation. This process is known as selective oxidation. Most of the Fe, Ni, and Co alloys rely on the selective oxidation of Cr to  $\text{Cr}_2\text{O}_3$  scale for oxidation resistance (Wright and Dooley, 2010; Boinovich et al., 2011; Del et al., 2012; Chatha et al., 2012; Sadique et al., 2000; Stott et al., 1995; Gasik et al., 1970; Hetmanczyk et al., 1979). Some high-temperature alloys use Al to form  $\text{Al}_2\text{O}_3$  scale for oxidation resistance (Sadique et al., 2000; Stott et al., 1995; Masalski et al., 1999; Yamamoto et al., 2007; Dunning et al., 2002).

Another important use of internal oxide particles is in the mechanical strengthening of alloys. So-called oxygen dispersion strengthened alloys, in which small (nanosized) particles

of rare earth titanates and related oxide phases appear to slow the movement of defects and the propagation of cracks in alloys operating at high temperature (Wright et al., 2001; Kamise et al., 1967; Ukai et al., 2002; Chen and Dong, 2011; Oksiuta et al., 2011; Tang et al., 2012; Voevodin et al., 2011; Zhong et al., 2012; Zhou et al., 2012). The thermodynamics and kinetics of such precipitate formation reflect complex phenomena currently under active investigation.

## 2.7 Volatile Oxides

Some oxides exhibit high vapor pressure above 1000°C. Hence, oxide scales become less protective, when their vapor pressure is high. Cr, Mo, W, V, Pt, Rh, and Si are metals for which volatile oxygen-bearing species are important at high temperature. Oxidation of Pt and Pt group metals at high temperature is influenced by oxide volatility in that the only stable oxides are volatile. This results in continuous mass loss (Jehn, 1984). Alcock and Hopper studied the mass loss of Pt and Rh at 1400°C as a function of oxygen partial pressure (Alcock and Hooper, 1960). The gaseous species were identified as PtO<sub>2</sub> and RhO<sub>2</sub>. These results have additional significance because; Pt and Pt-Rh wires are often used as thermocouples, furnace windings, electrical contacts, and sample holders to support specimens during high-temperature experiments. It is notable that although W and Mo are high melting and show low volatility in the absence of oxygen, their oxides are low melting and extremely volatile (Table 2.6).

Formation of SiO<sub>2</sub> on silicon-containing alloys and ceramics results in very low oxidation rates. However, a significant pressure of SiO is in equilibrium with SiO<sub>2</sub> and Si at oxygen pressures near the dissociation pressure of SiO<sub>2</sub> (Bronson and Chessa, 2008; Rocabois et al., 1996). This results in a rapid flux of SiO away from the specimen surface and the SiO<sub>2</sub> coating is no longer protective (Wagner, 1958, 1965). In the presence of carbon (graphite or other carbon source), the carbothermic reduction of silica by the reaction SiO<sub>2</sub> (solid) + C

**TABLE 2.6**

Melting Point and Boiling Point of Some Representative Metals and Oxides

Materials	Approximate Melting Point (°C)	Approximate Boiling or Decomposition Point (°C)
Mo	2610	5560
MoO <sub>3</sub>	795	1155
W	3407	5727
WO <sub>3</sub> <sup>a</sup>	1470	1700
Pt	1772	3800
PtO	—	d.550
PtO <sub>2</sub>	—	d.650
IrO <sub>2</sub>	—	d.1124
Rh	1966	3727
Rh <sub>2</sub> O <sub>3</sub>	—	d.1100
Si	1414	3250
SiO	1700	1880
SiO <sub>2</sub>	1600	2230

<sup>a</sup> Significantly volatile at 800–1000°C.

(solid) = SiO (gas) + CO (gas) becomes thermodynamically favorable above about 1500°C (Dhage et al., 2009; Komarov et al., 2005; Shimoo et al., 1995; Tolstoguzov, 1989). In the presence of low concentrations of oxygen, the formation of SiO from silicon nitride, silicon carbide, and polymer-derived ceramics in the Si-O-C-N system (Greil, 1998) also becomes a major mechanism of corrosion. Thus, silica and carbon are basically incompatible at high-temperature and SiO as a gaseous species limits the protective effect of silica coatings, especially under low oxygen fugacity (Wagner, 1958; Opila and Jacobson, 1995). The presence of water vapor (steam) also enhances corrosion and vaporization of silica coatings (Deal and Grove, 1965; Hashimoto, 1992; Opila, 2004).

Similar volatility problems are encountered at high temperature for boron-containing materials such as the nitride, BN. Oxidation of pure BN is complex and highly dependent on the microstructure of the BN and water vapor content in the gas stream. High deposition temperature chemically vapor deposited boron nitride (CVD BN) is the most desirable, but may lead to problems in composite fabrication. As BN and SiC oxidize, there are numerous interactions between the oxidation products. It has been identified three basic mechanisms of formation of borosilicate glass, gettering of oxygen by SiC and preservation of the BN, and volatilization of the BN via  $B_2O_3$  and  $H_xB_yO_z(g)$  formation (Jacobson et al., 1999; Segal, 1984).

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## 2.8 Summary

This overview summarizes the ranges of use and thermodynamic driving forces for failure of high-temperature materials. These constraints must be taken into account when designing systems for high-temperature use. Knowledge of the fundamental chemistry and consideration of all possible chemical interactions is essential to avoid unexpected and possibly catastrophic failure of materials at 1000°C and above, where the rates of reactions can be rapid and thermodynamic equilibrium can be established rapidly.

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# 3

## *Refractory Metals, Ceramics, and Composites for High-Temperature Structural and Functional Applications*

Jeffrey W. Fergus and Wesley P. Hoffmann

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### **3.1 Introduction**

High temperatures offer advantages or are required for many applications. Materials for a specific high-temperature application are chosen based on their properties at the application temperature, the environment in which they will function, the time at temperature, and the frequency at which they will cycle between temperatures. In this chapter, rather than focusing on a particular group of materials or a particular temperature range, a brief overview of the various classes of high-temperature materials will be given and then some of the general issues associated with high-temperature applications will be discussed and illustrated with some specific examples.

The definition of what constitutes a high temperature is relative as it depends on the situation or application and is different for different materials. For example, high-temperature superconductors operate at less than  $-100^{\circ}\text{C}$ , while in the rocket propulsion community a rocket nozzle is not considered to be at high temperature until it reaches  $3100^{\circ}\text{C}$ . Similarly,  $550^{\circ}\text{C}$  is a very high operating temperature for aluminum which melts at  $660^{\circ}\text{C}$ , but a low temperature for tungsten, which does not melt until  $3400^{\circ}\text{C}$ .

#### **3.1.1 Advantages of and Needs for High Temperatures**

High temperatures are generated in a variety of applications, such as in high-speed aircraft where friction generates heat. Materials processing, such as casting and heat treatment, require materials to generate the heat and to contain the materials. Energy conversion processes often involve high temperatures—nuclear fusion, for example, occurs only at very high temperatures. In other cases, high temperatures are desired because of improved performance, such as in the conversion of thermal energy into mechanical energy, the efficiency of which is limited according to the Carnot cycle. Similarly, reaction rates increase at high temperatures, so high temperatures are used for the conversion of chemical energy into electrical energy or chemicals into other chemicals.

#### **3.1.2 Challenges Associated with High Temperatures**

High temperatures create additional constraints in the design and selection of materials. The phases used are often not the equilibrium phases, in which case, phase stability can be an issue. This can include decomposition of the material into a more stable phase(s) or reaction with a gas in the surrounding environment or reaction with another condensed phase present in the system. Even if the phase is the equilibrium phase, changes in the morphology can occur. For example, high surface areas are needed for catalysts and electrodes. Similarly, fine microstructures often provide good mechanical properties. These high-interfacial-area structures are inherently unstable due to the high surface energy associated with the large interfacial area and can coarsen during high-temperature use.

Synthesis and the processing of high-temperature materials can also be a challenge. Typical material processing techniques, such as casting and sintering, are performed above the application temperature, which is clearly a challenge for high-temperature materials. In addition to synthesis, fabrication, and shaping of the individual materials, joining of high-temperature materials can be difficult.

Performance of materials can also be degraded at high temperatures. This can include mechanical properties, such as strength, or long-time deformation by creep. In addition, functional properties related to transport properties or transduction are temperature dependent.