

Ultrahigh-Temperature Materials for Jet Engines

J.-C. Zhao and J.H. Westbrook, Guest Editors

Abstract

This introductory article provides the background for the September 2003 issue of *MRS Bulletin* on Ultrahigh-Temperature Materials for Jet Engines. It covers the need for these materials, the history of their development, and current challenges driving continued research and development. The individual articles that follow review achievements in four different material classes (three *in situ* composites—based on molybdenum silicide, niobium silicide, and silicon carbide, respectively—and high-melting-point platinum-group-metal alloys), as well as advances in coating systems developed both for oxidation protection and as thermal barriers. The articles serve as a benchmark to illustrate the progress made to date and the challenges ahead for ultrahigh-temperature jet-engine materials.

Keywords: coatings, composites, ductility, jet engines, oxidation, oxides, platinum-group-metal alloys (PGM alloys), silicides, strength, structural materials, thermal-barrier coatings, toughness, ultrahigh-temperature materials.

This year marks the centennial of the Wright brothers' first flight. In the second half of the last century, aircraft powered by jet engines came to dominate both civilian and military flights, and they continue to have tremendous impact on the economy and on our lives (e.g., aircraft turbine engines are the single largest U.S. export product).

The history of the jet engine goes back much farther than one would suppose. Jacques Etienne Montgolfier was the first to propose reaction propulsion for aircraft in 1783. His concept was intended for a balloon rather than an airplane and more for steering than main propulsion. The first patent for a turbine engine appeared in 1791; it was intended for use on a horseless carriage (automobile). Charles de Leuvié first suggested the idea for a jet-powered monoplane in 1865, but it was not until 1928 that Frank Whittle, a 21-year-old Royal Air Force cadet, advanced the idea of jet propulsion for aircraft in a published thesis. Although his concept was rejected by the authorities of the time, he persevered and by April 12, 1937, had built and

successfully tested his first turbo-jet engine. Whittle's engine first powered an airplane (the Gloster E2) on May 15, 1941. Meanwhile, an independent parallel effort was going forward in Germany. Hans von Ohain obtained a patent for a jet engine on November 10, 1935. With backing from Ernst Heinkel, he built the He S3B engine, which successfully powered an airplane, the He 178, on August 27, 1939. Both of these developments came too late to have a significant impact on World War II, although some military jets were flown in the 1940s. The commercial significance of the new mode of power was apparent, and in 1952, the British Overseas Airways Co. (BOAC) inaugurated the first scheduled jet passenger service. In 1992, Ohain and Whittle shared the Draper Prize for "early jet development and contributions to mankind." Readers may be interested in their biographies^{1,2} and in another book³ that clearly explains the fundamentals of a jet engine.

The need in any engine for materials with strength at high temperatures was recognized early, but the first step was to

use alloys already known for their modest high-temperature strength and oxidation resistance, such as the Ni-Cr alloys introduced by Marsh in 1906. Only in the late 1930s and early 1940s, with the introduction of the jet engine, was a concerted research effort launched, principally by the Mond Nickel Co. in the United Kingdom, to develop alloys particularly for this purpose. The history of this development was sketched in a recent review.⁴ Present-day alloys for this application, Ni-based superalloys, evolved during a period of 70 years or more through small incremental changes contributed by engine manufacturers, materials producers, and materials research and development specialists. These alloys are composed of Ni₃Al (γ') precipitates in a Ni (γ) matrix with admixtures of 10–12 other elements dissolved in one or both of the major phases. The current alloys operate for thousands of hours under loads on the order of 140 MPa at 85% of their melting point. It is now clear that neither the increasing sophistication of our understanding of how such performance is achieved, nor the possibility of further tinkering with composition or processing, nor advances in turbine design (e.g., more complex cooling systems) will yield the improvements demanded by engine designers. We still need substantially improved high-temperature materials that can only come from a completely different materials class.

The jet engine is a very complex yet operationally simple device. Figure 1 shows a GE 90-115B engine, the most powerful jet engine in the world. It consists essentially of a stationary, hour-glass-shaped, cylindrical case on which all of the vanes (nozzles) and the combustion chamber (combustor) are attached, and a rotating mandrel on which a series of disks (rotors, wheels) are mounted. Attached to the peripheries (perimeters/rims) of the disks are the blades (either compressor blades or turbine blades). The vanes duct the air into appropriate directions to effectively propel the blades. Alternating rows of vanes and blades are arranged in both the compressor and turbine sections. As the air is compressed, its temperature rises; it is then mixed with fuel and burned in the combustor to raise the temperature. The high-temperature, high-pressure (high-energy) gas coming out of the combustor is ducted by the first-stage, high-pressure turbine (HPT) vanes to propel the first-stage HPT blades. The efficiency and performance of the jet engine are strongly dependent on the highest temperature in the engine—the inlet temperature of the HPT—and it is the high-temperature capability of these parts that is critical. To achieve higher thrust, higher operating

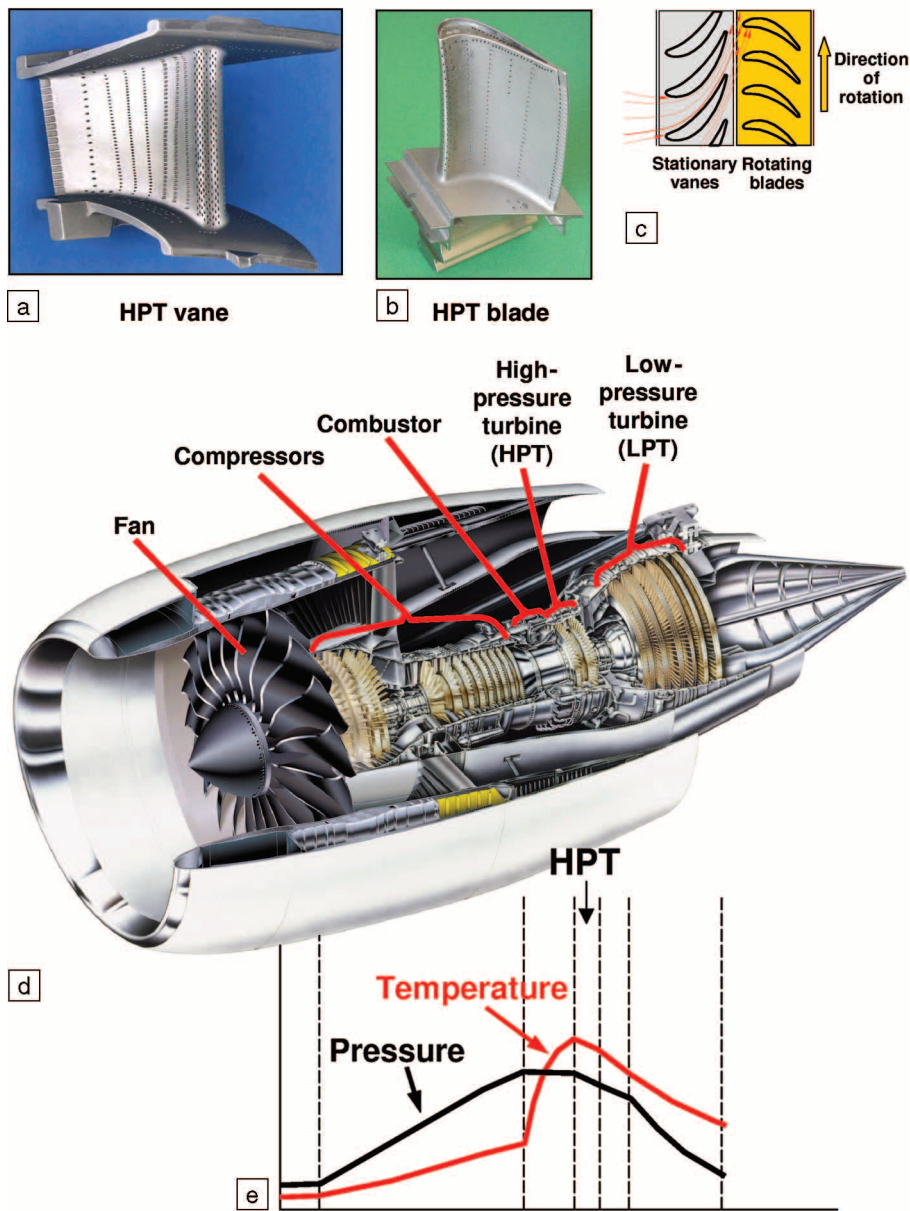


Figure 1. (a), (b) Photographs of a high-pressure turbine (HPT) vane and a HPT blade of a jet engine. (c) Schematic arrangement of the stationary vanes relative to the rotating blades within the engine. (d) Illustration of the GE 90-115B jet engine, showing its various components. (e) Pressure and temperature trends from the front to the back of the engine.

temperatures must be realized. To achieve higher efficiency, engines must be made significantly lighter without loss of thrust. In either case, it is obvious that completely new families of materials must be developed, ones with higher melting points and greater intrinsic strength.

There are only four categories of materials that can be considered: refractory metals, monolithic ceramics, intermetallic compounds, and composites (natural or synthetic).

The first category can be immediately ruled out. None of the refractory metals is sufficiently oxidation-resistant, and all of them, with the exception of chromium, are substantially denser than present-day Ni-based alloys. Chromium, while having the advantage of a lower density than nickel, is only marginally tough at room temperature and is subject to nitrogen embrittlement when exposed to air at high temperatures. Klopp⁵ and Ro et al.⁶ summarized the progress made with Cr-based alloys; these

alloys are currently not considered good prospects for meeting the need. Perhaps significantly, Cr-based alloys were not covered in Sims et al.'s 1987 work, *Superalloys II*.⁷

Many monolithic ceramic materials possess good strength at jet-engine operating temperatures. However, their inherent brittleness poses a significant challenge in withstanding the rigors of assembly and the impact damage caused by foreign objects that may pass through the engines in operation. These materials will have limited applications in turbine engines without further development of improved materials and innovative system architectures.

Thus, we focus on the remaining two classes of potential materials: intermetallic compounds and composites. It is these two groups that are the subjects of the detailed reviews that follow in this issue of *MRS Bulletin*.

There are three families among the intermetallics that have received serious attention for jet-engine applications: γ -TiAl, NiAl, and the platinum-group metal (PGM) compounds. TiAl is considered from an engineering point of view to be the most mature intermetallic for jet-engine applications. Yet its modest melting point ($\sim 1500^\circ\text{C}$) precludes it from use in high-temperature blades and restricts it to the low-pressure turbine and static parts of the engine. After more than 20 years of effort on TiAl,⁸⁻¹¹ it is not yet used in commercial jet engines, despite the fact that a 1993 engine test of a low-pressure fan with 98 TiAl blades was successful. The problems that remain include low room-temperature ductility (1–2%), low fracture toughness, high stress-sensitivity of fatigue life, and high manufacturing cost for finished parts.

NiAl has a number of attractive properties for jet-engine applications, such as a high melting point ($\sim 1650^\circ\text{C}$), good thermal conductivity, low density, and intrinsic oxidation resistance. With suitable alloying (Ta + Cr), good strength properties at temperatures higher than 1000°C can be achieved. Alloy parts based on this intermetallic have been successfully made by a variety of processes (e.g., investment casting, powder metallurgy, hot extrusion, and injection molding). Tests for application as static parts for stationary turbines have been successful. In NiAl alloy development for jet-engine applications, both directionally solidified eutectics and polycrystalline multiphase structures have been explored. Serious consideration for engine applications will require better toughness at room temperature and higher creep strength at high temperatures. Recent summaries of the status of NiAl for engine applications may be found in Mir-

acle and Darolia,¹² Noebe and Walston,¹³ and several other papers.^{14–17}

The PGM-based intermetallic alloys that have been studied for possible application as high-temperature structural materials fall into two classes: those that are isomorphous with Ni₃Al (e.g., Pt₃Al), and those that are isomorphous with NiAl (e.g., RuAl). In both cases, the advantages of PGM-based intermetallics over Ni-based superalloys are a significantly higher melting point (~1500°C for Pt₃Al and ~2100°C for RuAl) and inherent oxidation resistance, albeit with some increase in density. Recent reviews of these alloys are presented by Wolff et al.^{18,19} and Yamabe-Mitarai et al.²⁰ Most of the attention has been focused on Pt- and Ru-based compounds, but there have been some studies of Ir-based²¹ and Rh-based²² materials. Progress toward the desired properties has been either by alloying to improve strength and reduce density or by oxide-dispersion strengthening (ODS). In this issue, Cornish et al. review current activities and achievements with each approach.

Composite materials are defined²³ as a macroscopic combination of two or more distinct materials having a recognizable interface between them. More particularly, structural composites are those in which a continuous matrix phase bonds and provides toughening characteristics to an array of pieces of a stronger, stiffer reinforcement phase. Structural composites may be formed by artificially bringing together a suitable combination of matrix and reinforcement phase (as in the case of glass-fiber-reinforced polymers) or produced naturally by suitable processing of a carefully selected composition (so-called *in situ* composites). All three composite systems reviewed here fall into this category of *in situ* composites. All are silicon-rich, which lowers density and provides a basis for oxidation resistance, but they differ in the nature of the reinforcing phase or phases. Dimiduk and Perepezko review achievements with *in situ* composites in the Mo-Si-B system, Bewlay et al. address the Nb-Ti-Cr-Si system, and Naslain and Christin cover SiC/SiC ceramic-matrix composites (CMCs). The oxidation behavior and the density-normalized strength of these materials are compared in Figures 2 and 3.^{24–37} The reader is cautioned that the data for the different materials were not necessarily obtained under comparable conditions and that all materials shown are under continuous development with progressively improving properties.

Although all of the materials discussed in this issue show promise as ultrahigh-temperature materials for advanced jet engines, there is no clear winner among them

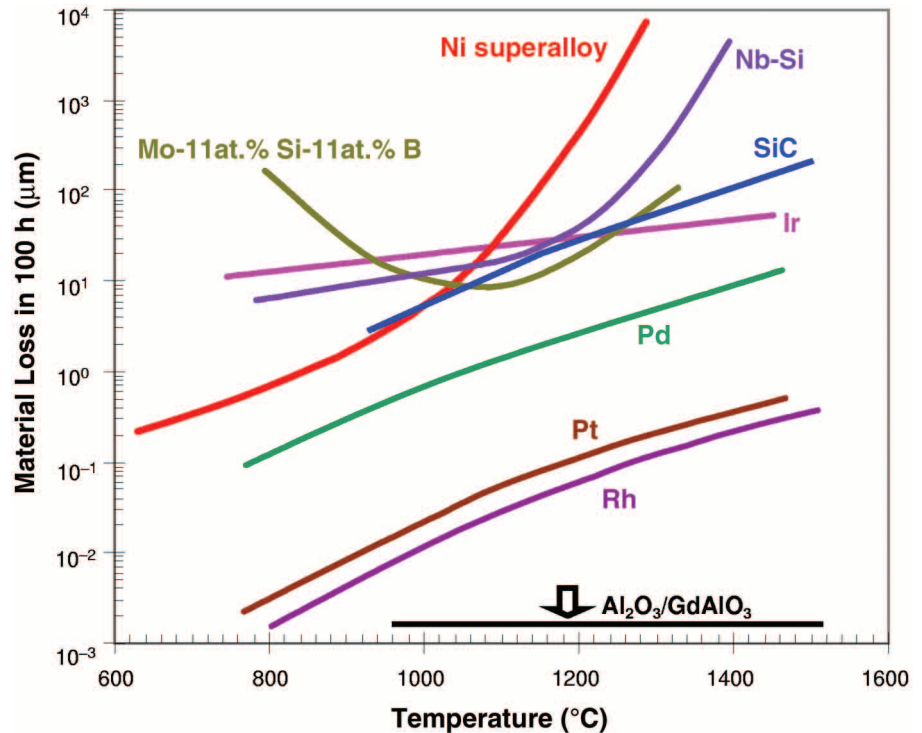


Figure 2. The oxidation/recession rate of various ultrahigh-temperature materials discussed in this issue of MRS Bulletin. The data were obtained from References 24–29. The best published data were plotted for each class of materials. The recession rate is a good figure of merit for oxidation resistance, as it measures the material loss in thickness by oxidation at certain temperatures and time periods. The material loss is usually by formation and spallation of a thermally grown oxide scale, or by evaporation of the metal and oxide in the case of platinum-group metal alloys and Mo-Si-B. The results on Mo-Si-B are only for one alloy (Mo-11at.%Si-11at.%B) and are only preliminary, sensitive to a variety of processing, composition, and microstructure variables. The SiC data were used as a proxy for ceramic-matrix composites (CMCs), since the CMC data were not available in the literature. The data reported here for SiC were an average of both lean- and rich-burn combustion conditions.²⁸ The oxidation data were not obtained under identical conditions, therefore this figure is only intended to show the approximate present performance for each class of materials; such data are likely to get better with further materials development.

so far. Relatively speaking, the development of Mo-Si-B, Nb-silicide-based composites, and PGM-based alloys is still in its infancy, while the development of CMCs has a much longer history. Each class of materials has its own merits and drawbacks, as briefly summarized here and discussed in the respective articles.

■ **SiC/SiC Ceramic-Matrix Composites** are the closest to the long-term engine testing stage; several engine tests with CMCs as combustion chambers have been performed on land-based gas turbines, and similar efforts for jet engines are currently under way. Their strength is relatively low, even on a density-normalized basis. For well-designed systems, the good impact resistance and stability at high operating temperatures make this system an attractive option; significant design effort will be required to take full advantage of the

properties as well as to master the challenges posed by mating CMCs with metallic components. Significant progress has been made in environmental-barrier coatings to combat the SiO₂ evaporation problem in high-velocity water-vapor environments. Cost, reliability, estimation of component life, and the manufacture of complex shapes are among the challenges requiring continued attention and development.

■ **Nb Silicide Composites** show good oxidation resistance, good resistance to peeling (intermediate-temperature pulverization), reasonable fracture toughness, good fatigue resistance, good high-temperature strength, good impact resistance, and can be cast reasonably well. Good coatings have also been developed for these composites. However, combining high oxidation resistance with high strength in a

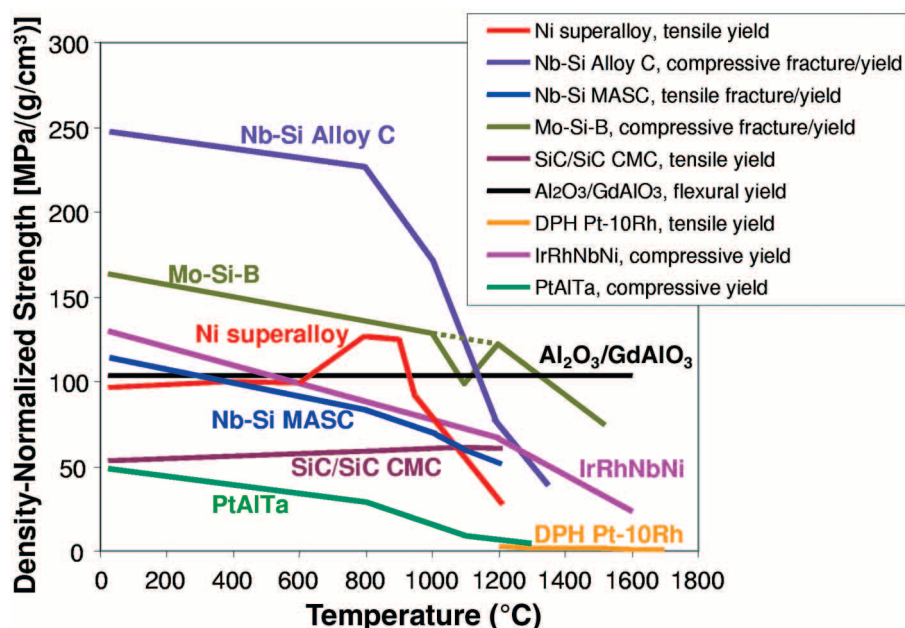


Figure 3. Comparison of the density-normalized strength of various ultrahigh-temperature materials. The data were obtained from References 30–37 and the articles published in this issue of MRS Bulletin. The best published data for each class of material are plotted here. Some of the strength data are from compression and bending tests. The results on Nb silicide composites, Mo-Si-B, and CMCs are only preliminary, and the low-temperature data are mostly elastic-fracture strength, which is very sensitive to defects and microstructure. This figure is intended only to show the best published performance so far for each class of materials. The MASC (metal and silicide composite) alloy has a composition of Nb-25Ti-8Hf-2Cr-2Al-16Si. Nb-Si Alloy C is an alloy patented by General Electric Co. and is described in more detail in the article by Bewlay et al. in this issue. DPH Pt-10Rh is a “dispersion-hardened” (DPH) platinum alloy containing 10 at.% Rh. For more on platinum-group-metal alloys, see the article by Cornish et al. in this issue.

single composition remains a problem, as does manufacturability.

■ **Mo-Si-B Composites** exhibit excellent high-temperature creep strength, outstanding high-temperature yield strength, and excellent oxidation resistance at temperatures above 1000°C. Among their problems are less-than-desirable oxidation resistance at intermediate temperatures, poor manufacturability, poor fatigue resistance, poor impact resistance, and low fracture toughness. Improvements on these fronts are required.

■ **PGM-Based Alloys** show excellent oxidation resistance with low amounts of alloying additions. Most of the alloys have low strengths (both yield and creep rupture), very high density, and high cost. The Ir-based alloys show very high strength, but they no longer have the oxidation resistance of the PGMs due to high alloying. The development of PGM-based alloys is still in its infancy, and there is the potential for high strength by both alloying and ODS. In order for them to be used in jet engines, innovative designs will be required to take advantage of the excellent properties of

PGM-based alloys while avoiding the problems of high density and cost.

The strength data of Al₂O₃/GdAlO₃ Eutectic Composites are shown in Figure 3 as a benchmark of oxide-oxide composites. Initial work on this material²⁹ shows great high-temperature strength, reasonable fracture toughness (5 MPa m^{1/2} at room temperature and 13 MPa m^{1/2} at 1600°C)³⁸ and great oxidation resistance (no loss of material even after exposure at 1700°C for 1000 h). But it has a serious drawback—a lack of the thermal-shock resistance required to survive engine startups and shutdowns. It would be a good potential high-temperature material if the thermal-shock-resistance problem were solved, either by engine design or by material improvement. In addition, the high strength of this material only exists in the melt-grown, *in situ* composite where no glassy phase exists along interfaces. It would greatly improve the manufacturability of this composite if formation of the glassy phase during a sintering process could be avoided, thus making complex, near-net-shape blades possible.

For a bare material to survive in the oxidative environment of a high-temperature, high-velocity gas stream within a HPT, it needs either to form a protective oxide scale or to be virtually inert, as are the precious metals. Two protective oxides, Al₂O₃ and SiO₂, are the best candidates as oxide scales. It is this fact that dictated the basic compositions of the composite materials reviewed here. SiO₂ grows much slower than Al₂O₃ at high temperatures, thus conferring a clear advantage, but it evaporates more quickly in a high-velocity, moist environment. Compositional modification of the substrate materials has not yielded an attractive combination of oxidation resistance and high-temperature strength. Thus, it is concluded that all prospective new materials for jet-engine blades will require coatings to achieve acceptably long life. These coatings are quite complex materials systems. They are designed to serve two main functions: oxidation protection and thermal protection of the substrate material. Other layers may be included to provide auxiliary functions: bond coats between coating layers or between coating and substrate, or diffusion barriers to prevent degradation of either substrate or coating by inward or outward diffusion of components. A series of recent symposia chaired by Dahotre³⁹ has recorded progress in this area. In the final article in this issue, Nicholls describes the current status of the field.

But what is the future? Despite the progress made in understanding the problems confronting high-temperature structural materials and the ingenious developments in composition selection and processing for new base materials, the fact remains that none of the systems described here is in use in aircraft flying today. Continued developments will probably produce some further property improvements, but whether they will be enough to instigate wide usage is difficult to say at this point. It is critical to have a combined effort by materials people and designers to learn to work with low-ductility materials. On the materials side, we need materials and process improvements that will increase the consistency and reliability of performance, even at low ductility and toughness levels; and on the design side, new concepts must be developed that are more forgiving of lower-ductility materials. An alternate route to success may be to explore completely new base systems, perhaps ternary or quaternary compounds.

For those who are new to this subject field, we provide this list of suggested readings. Superalloys are covered in two monographs, those of Sims et al.⁷ and of Donachie and Donachie,⁴⁰ as well as in the

recurring Seven Springs Conferences on Superalloys volumes.⁴¹ Intermetallic compounds are treated in monographs by Sauthoff⁴² and by Stoloff and Sikka,⁴³ as well as in great detail in the three-volume treatise edited by Westbrook and Fleischer,⁴⁴ and in a series of Materials Research Society symposia proceedings.⁴⁵ Composites are covered in considerable detail in the recent *ASM Handbook*, Vol. 21.⁴⁶ Finally, the International Symposium on Structural Intermetallics series, three of which have been published so far,⁴⁷ considers composites, intermetallics, and other types of high-temperature structural materials.

Background information and tutorials on jet engines and advanced high-temperature materials may also be found on the Internet. Some of these sites are

- Ultra-Efficient Engine Technology (www.ueet.nasa.gov/Engines101.html);
- Superalloys: A Primer and History (www.tms.org/Meetings/Specialty/Superalloys2000/SuperalloysHistory.html); and
- AZoM—Metals, Ceramics, Polymers, Composites, An Engineer's Resource (www.azom.com).

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Ji-Cheng (J.-C.) Zhao, Guest Editor of this issue of *MRS Bulletin*, is a materials scientist at the GE Global Research Center in Schenectady, N.Y., where he has worked since 1995. His research focuses on the design of advanced alloys and coatings as well as hydrogen-storage materials. His particular emphasis is on phase diagrams, thermodynamics, diffusion, and composition–structure–property relationships. He developed a diffusion–multiple approach for the rapid mapping of phase diagrams and phase properties.

Zhao received his BS (1985) and MS (1988) degrees in materials from the Central South University, China, and his PhD degree in materials from Lehigh University (1995). He has received several honors, including the Geisler Award from the Eastern New York Chapter of ASM International and the Hull Award from GE Global Research, and he was elected a fellow of ASM International in 2003. Zhao has published approximately 45 papers and co-edited one book. He also holds 17 U.S. patents with about 20 more pending and is an associate editor for the *Journal of Phase Equilibria*.

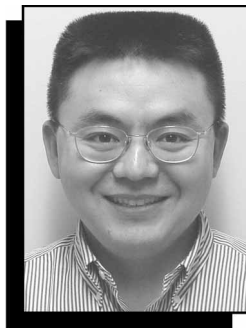
Zhao can be reached at the GE Global Research Center, K1-MB239, One Research Circle, Niskayuna, NY 12309, USA; tel. 518-387-4103, fax 518-387-6232, and

e-mail zhaojc@research.ge.com.

Jack H. Westbrook, Guest Editor of this issue of *MRS Bulletin*, is owner and principal consultant of Brookline Technologies, a consulting firm in Ballston Spa, N.Y. Westbrook consults both on materials and technical information systems. He was an early pioneer in research on intermetallic compounds as potential high-temperature structural materials and has edited six volumes of collected works on this topic.

Westbrook received BMetEng and MMetEng degrees from Rensselaer Polytechnic Institute and a ScD degree in metallurgy from the Massachusetts Institute of Technology. He joined General Electric's R&D Center in 1949, where he was engaged in materials research and program planning for over 20 years. In 1971, he was named manager of Materials Information Services, then a unit of Corporate Consulting, but subsequently transferred to the R&D Center. After retiring from GE in 1985, Westbrook and another ex-GE colleague established the consulting firm Sci-Tech Knowledge Systems, which specialized in studies of technical information systems. When this firm dissolved in 1991, Westbrook founded Brookline Technologies.

He is a fellow of four

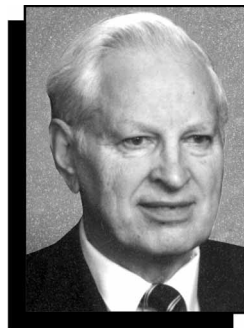


Ji-Cheng (J.-C.) Zhao

and a member of the National Academy of Engineering. He has received numerous national and international awards for his work. Two of these, ASM's Campbell Lecture and their Sauveur Achievement Award, were specifically for his work on intermetallics. Westbrook has a strong interest in the history of science and technology and has published extensively in this field as well. For several years, he has served MRS as a member of the *MRS Bulletin* editorial board and as a book reviewer.

Westbrook can be reached at Brookline Technologies, 5 Brookline Road, Ballston Spa, NY, 12020-3523, USA; tel. 518-885-8840 and e-mail jackwestbrook@earthlink.net.

Bernard P. Bewlay is a member of the scientific staff at General Electric Global Research in Schenectady, N.Y. His work is focused on fundamental and applied research of processing–structure–property relationships in



Jack H. Westbrook

high-temperature materials, refractory metals, refractory-metal composites, coatings, and titanium alloys. After receiving his DPhil degree in metallurgy and materials science from Oxford University in 1987, he joined Rolls-Royce, moving to GE Global Research in 1988. He is a member of the Materials Research Society, the Microscopy Society of America, and the Institute of Materials. He is also a fellow of ASM International. He has published more than 100 papers and holds 32 patents.

Bewlay can be reached at GE Global Research Center, K1-MB271, One Research Circle, Niskayuna, NY 12309, USA; tel. 518-387-6121, fax 518-387-5576, and e-mail bewlay@crd.ge.com.

François Christin is program engineer and manager of ceramic-matrix composites at Snecma Propulsion Solide (SPS) in Le Haillan, France. He graduated in 1975 from ENSCT (Toulouse)



Bernard P. Bewlay

and in 1979 obtained his PhD degree from Université Bordeaux 1.

After graduation, Christin started working for SEP. For 10 years, he was in charge of the development and industrialization of a new process executed during his PhD thesis known as chemical vapor densification of silicon carbide. He then continued as manager for research and development in composite materials for 10 years, during which time he developed a new materials family with his team and optimized characterization methods and modeling. Christin is currently in charge of the Research and Technologies Program at Snecma Moteurs (Aeronautic and Space Engines).

Christin can be reached at Snecma Propulsion Solide, Les Cinq Chemins, 33187 Le Haillan, France.

Lesley A. Cornish has been Head of the Advanced Materials Group in the Physical Metallurgy Division at Mintek (Randburg, South Africa),

since 2001 as well as an honorary professor at the University of the Witwatersrand in Johannesburg. From 1989 to 2001, she lectured at the University of the Witwatersrand, and before that (1985–1989), she worked for the United Kingdom Atomic Energy Authority.

Cornish studied metallurgy and materials at the University of Birmingham and also obtained her PhD degree there. Her interests are in the calculation and experimental derivation of phase diagrams, the relationship of structure and properties, and the development of alloys for special applications. Among other areas, she has worked with platinum-group-metal phase diagrams, platinum-based alloys, additions of vanadium to WC-Co hard metals, and additions of PGMs to stainless steels.

Cornish can be reached at the Physical Metallurgy Division, Mintek, Private Bag X3015, Randburg, South Africa; tel. 27-(0)-11-709-4474; fax 27-(0)-11-709-4480, and e-mail lesleyc@mintek.co.za.

Dennis M. Dimiduk is the research leader for advanced metallics at the Materials and Manufacturing Directorate of the Air Force Research Laboratory in Dayton, Ohio. He leads exploration and basic research on high-temperature structural alloys, and his work has sought an understanding of dislocation mechanisms in intermetallic alloys. For more than a decade, Dimiduk's work focused on inserting the γ -titanium aluminides into aerospace service and exploring refractory-metal silicides as high-

temperature structural alloys for propulsion systems. His research also seeks to understand the influence of chemistry on microstructural evolution and deformation in alloys through simulation methods. Those techniques have been applied to advance γ -titanium aluminides, and are now being directed toward superalloys.

Dimiduk received his BS in materials science and engineering from Wright State University and his MS and PhD degrees in metallurgical engineering and materials science from Carnegie Mellon University. For 26 years, he has been with the AFRL (and its predecessors). He has authored or co-authored more than 120 technical papers and 10 patents on advanced metals and processes. He is a member of the editorial board for the journal *Intermetallics* and is an adjunct professor at Wright State and Ohio State. Dimiduk is a fellow of ASM International and of the AFRL. Currently, he is continuing to investigate computational materials science and engineering methods for accelerated insertion of metals into service.

Dimiduk can be reached at USAF Wright Laboratory, WL-MLLM, 2230 10th Street, Suite 1, Bldg. 655, Wright Patterson Air Force Base, OH 45433, USA; tel. 937-255-9839, fax 937-255-3007, and e-mail dennis.dimiduk@wpafb.af.mil.

Bernd Fischer is a professor of materials science at the University of Applied Sciences Jena in Germany. He studied materials technology at the Technical University Chemnitz and received his doctorate degree in 1971. After that, he



François Christin



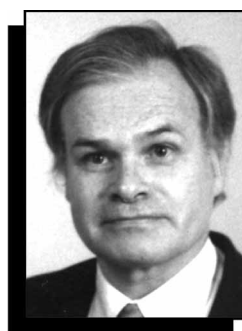
Lesley A. Cornish



Dennis M. Dimiduk



Madan G. Mendiratta



Roger Naslain



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started to work in the field of high-temperature materials, especially platinum-group metals, at the Friedrich Schiller University. He investigated the corrosion resistance of platinum materials in glass-melting plants and the interaction between molten glass and platinum materials, in particular, the influence of molten glass on crystal structure and on the high-temperature properties of platinum alloys. After more than 25 years of research and teaching at Jena, Fischer was awarded the chair of materials science in 1992. He was dean of the Faculty of Materials Technology from 1992 to 1994 and pro-rector for research from 1994 to 1997. During the last few years, his research focused on the development and characterization of platinum alloys, especially oxide-dispersion-hardened platinum materials. He has also investigated mechanical high-

temperature properties (stress rupture strength and creep behavior) of refractory metals (rhenium, tungsten, molybdenum, and their alloys) at temperatures in the range of 1500–3000°C.

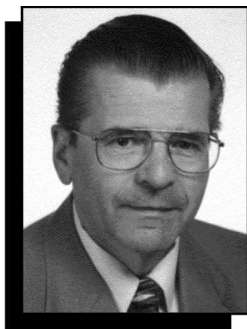
Fischer can be reached at FH Jena—University of Applied Sciences, Dept. of Materials Technology, Carl-Zeiss-Promenade 2, D-07745 Jena, Germany; tel. 49-(0)-364-120-5475; fax 49-(0)-364-120-5476, and e-mail bernd.fischer@fh-jena.de.

Melvin R. Jackson has been a researcher in the Ceramic and Metallurgy Technology Laboratories of the General Electric Global Research Center in Schenectady, N.Y., since 1972. After receiving a PhD degree in metallurgy and materials engineering from Lehigh University, he worked with INCO for a year. He has concentrated his research on high-temperature systems,

phase equilibria, interdiffusion, and interaction. His current areas of interest include the behavior of refractory-metal composites, coatings, and metallic interconnects for solid-oxide fuel cells. He is the author or co-author of 105 papers and articles, holds 111 U.S. patents, and was awarded GE's Coolidge Fellowship in 1995.

Jackson can be reached at GE Global Research, Rm. MB223, P.O. Box 8, Schenectady, NY 12309, USA; tel. 518-387-6362, fax 518-387-7495, and e-mail jacksmr@crd.ge.com.

John J. Lewandowski is currently the Leonard Case Jr. Professor of Materials Science and Engineering and Director of the Mechanical Characterization Facility at Case Western Reserve University, where he has been on the faculty since 1986. His publications and presentations number in excess of 150 and



Bernd Fischer



Melvin R. Jackson



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350, respectively, and are primarily in the areas of processing–structure–property relationships in ferrous and nonferrous engineering materials; the effects of superposed pressure on deformation and fracture; fatigue and fracture of intermetallics and composites, bulk metallic glass, and layered/laminated materials; deformation processing; and blast-resistant materials and structures. Lewandowski received his BS, ME, and PhD degrees in metallurgical engineering and materials science at Carnegie Mellon University, where he was a Hertz Foundation fellow. Two years were spent as a NATO postdoctoral fellow in the Department of Materials Science and Metallurgy at Cambridge University, England, working with J.F. Knott on fracture and fatigue of engineering metals. He was recently elected

an overseas fellow at Churchill College, University of Cambridge. Other honors include ASM fellow, the NSF Presidential Young Investigator Award, the SAE Ralph R. Teetor Educational Award, the ASM Bradley Stoughton Award for Young Teachers, the ASM Research Silver Medal, the CTSC Technical Educator Award, and the Charles Hatchett Award from the Institute of Metals for work on Nb.

Lewandowski can be reached at Case Western University, Dept. of Materials Science and Engineering, Charles White Metallurgy Bldg., Cleveland, OH 44106, USA; tel. 216-368-4234, fax 216-368-8618, and e-mail jjl3@po.cwru.edu.

Madan G. Mendiratta is director of the Materials and Processor Division at UES Inc. in Dayton, Ohio. In this capacity, he

provides technical and administrative management to a number of research programs for the U.S. Air Force. His research focus for the past several years has been on the development of materials for high-temperature structural applications in advanced jet engines. These materials include metallic and intermetallic complex multiphase systems. Mendiratta has conducted research on processing, phase relations, microstructural evolution, mechanical properties, and oxidation mechanisms. He has published more than 200 papers in internationally refereed journals, written three book chapters, and holds five patents. Mendiratta received his PhD degree in materials science and engineering mechanics from Rutgers University in 1970.

Mendiratta can be reached at UES Inc.,

Materials Research Division, 4401 Dayton-Xenia Road, Dayton, OH 45432-1894, USA; tel. 937-255-9832, fax 937-656-7292, and e-mail madan.mendiratta@wpafb.af.mil.

Roger Naslain is professor emeritus at the Université Bordeaux 1 in Pessac, France. Until September 2002, he was director of the Laboratory for Thermostructural Composites (LCTS), a joint institution involving the university, CNRS (the National Center for Scientific Research), Snecma, and CEA (the French Atomic Energy Commission). His research focuses on processing, materials design, and properties of ceramic fibers and ceramic-matrix composites and their application in the space and aeronautic industries. He is a member of the Academy of Ceramics (and laureate of its 2000 prize), Academia Europaea, the American Ceramic Society (fellow and associate editor), the European Ceramic Society, and the European Society for Composite Materials (former vice president). He created and co-chaired a series of International Conferences on High-Temperature Ceramic-Matrix Composites (Bordeaux, Santa Barbara, Osaka, Munich, and Seattle). He has edited nine books or special issues of scientific journals, published 300 articles, and holds 16 patents.

Naslain can be reached at the Laboratoire des Composites Thermostructuraux, UMR 5801 (CNRS-SNECMA-CEA-UB1), Université Bordeaux 1, 3 Allée de la Boétie, 33600 Pessac, France; tel. 05-56-844-

706 and e-mail naslain@lcts.u-bordeaux.fr.

John R. Nicholls is professor of coatings technology at Cranfield University in the United Kingdom. He has considerable experience in high-temperature surface engineering and corrosion of materials at high temperature and has been involved in coatings technology since 1978. He is a materials scientist who has undertaken work in the areas of coating deposition (PVD, CVD, and HIP surfacing), structure characterization, and the design of novel multilayered and graded structures. He has a strong interest in the stability of intermetallics as part of a coating system, the design of smart corrosion-resistant coatings, and the manufacture of low-thermal-conductivity thermal-barrier coatings. This has included studies of thermal conductivity in TBCs, the role of dopant additions and advanced processing, bond-coat oxidation, erosion, and foreign-object damage. John Nicholls is actively involved in the design of corrosion life models that take into account the stochastic nature of high-temperature corrosion processes. To this end, he has also carried out fundamental studies on oxidation, corrosion, and erosion mechanisms and their interactions. He has managed numerous research projects, published more than 170 papers, edited several books, and is the joint holder of two coating patents. He is a member of the Surface Engineering and High Temperature Materials Performance Committees of the Institute of Materials and immedi-

ate past chairman of the Institute's Surface Engineering Committee.

Nicholls can be reached at Cranfield University, Bldg. 61, Cranfield, Bedfordshire, MK43 0AL, UK; tel. 44-(0)-123-475-4039 and e-mail j.r.nicholls@cranfield.ac.uk.

John H. Perepezko is the IBM-Bascom Professor of Materials Science and Engineering at the University of Wisconsin—Madison. His research focuses on phase-transformation behavior, especially during the nucleation stage of reactions, microstructure–property relationships during materials processing, high-temperature intermetallic alloys and coatings, solidification, phase stability, modeling, and materials design. He received his PhD degree in metallurgy and materials science from

Carnegie Mellon University and has also worked at the U.S. Steel Research Laboratory. He was honored with the Forschungpreise from the Alexander von Humboldt Foundation. He is a fellow of ASM International and TMS and an editor for *Scripta Materialia*.

Perepezko can be reached at the University of Wisconsin—Madison, Dept. of Materials Science and Engineering, 1509 University Ave., Madison, WI 53706-1595, USA; tel. 608-263-1678, fax 608-262-8353, and e-mail perepezko@engr.wisc.edu.

P.R. Subramanian is a materials scientist at General Electric Global Research in Schenectady, N.Y. After obtaining his MS and PhD degrees in materials science and engineering from Iowa State University, he did postgraduate work at

Carnegie Mellon University. Prior to joining GE, he worked for UES Inc. for 12 years in the area of aerospace materials within the Air Force Research Laboratory at Wright-Patterson Air Force Base, Ohio. He has also served as an adjunct professor in mechanical and materials engineering at Wright State University, where he has developed and taught courses on high-temperature materials, corrosion, diffusion, and multicomponent phase diagrams. His current areas of research include processing–microstructure fundamentals in nanostructured metallic systems, structural applications of refractory-metal systems, and friction stir welding of aerospace alloys. Subramanian is a fellow of ASM International. He has over 70 publications in alloy development,

microstructure–property relationships, phase transformations, and processing, holds six U.S. patents, and is the co-editor of *Binary Alloy Phase Diagrams Handbook*, published by ASM International.

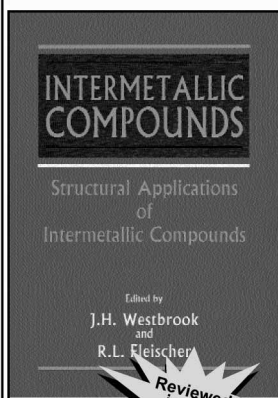
Subramanian can be reached at the GE Global Research Center, Schenectady, NY 12301, USA.

Rainer Völkl is a senior lecturer and senior researcher at the University of Bayreuth, Germany. His main scientific interests are the physical metallurgy and technology of platinum-group metals. Völkl studied materials science at the Technical University of Berlin and Ecole Central de Lyon, France. In 1997, he received a PhD degree in materials science for his work on convergent-beam electron diffraction and finite element simulation

of internal stress fields in nickel-based superalloys. From 1997 to 2003, he was at the University of Applied Sciences Jena and the Friedrich Schiller University in Jena, working together with Schott Glas and W.C. Heraeus GmbH & Co. on several R&D projects involving platinum, rhodium, and iridium alloys. For 2003 and 2004, Völkl will join the research group of Dr. Harada at the National Institute for Materials Science in Tsukuba, Japan, as a fellow of the Japan Society for the Promotion of Science.

Völkl can be reached at the University of Bayreuth, Dept. of Metallic Materials, Ludwig-Thoma-Strasse 36b, D-95440 Bayreuth, Germany; tel. 49-(0)-921-55-5553; fax 49-(0)-921-55-5561, and e-mail Rainer.Voelkl@uni-bayreuth.de. □

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