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Advanced Ceramics: A Critical Assessment of Wear and Lubrication

R. G. Munro and S. M. Hsu

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
(Formerly National Bureau of Standards)
Gaithersburg, MD 20899

January 1989

Sponsored by:
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ADVANCED CERAMICS: A CRITICAL ASSESSMENT OF WEAR AND LUBRICATION

TOPICAL REPORT
June 1986 - October 1986

Prepared by

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GRI Project Manager
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Materials Technology and Components

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RESEARCH SUMMARY

Title	Advanced Ceramics: A Critical Assessment of Wear and Lubrication
Contractor	Center for Advanced Materials The Pennsylvania State University GRI Contract Number: 5084-238-1302
Subcontractor	Ceramics Division National Institute of Standards and Technology CAM Contract Number: GRI-TPSU-NBS-1302-379
Principal Investigators	Stephen M. Hsu and Ronald G. Munro
Report Period	June, 1986 - October, 1986
Objectives	To assess the tribological issues, needs, and priorities for research on friction, wear, and lubrication of ceramic materials relevant to gas-fired prime movers.
Technical Perspective	Currently, small, but well established, markets exist for gas-fired reciprocating engines. The oil, gas, and agricultural industries use such engines to provide power to drilling operations, air compression, and fluid pumping. In these applications, the availability of the fuel may be a greater factor than efficiency in determining usage. Similarly, gas-fired turbine engines are used widely in power plants. In the latter application, reliability, lifetime, and long time intervals between maintenance are more important considerations than efficiency. Further, potential new markets exist, in both the near term and the far future, that could significantly expand the utilization of natural gas prime movers. In these potential markets, however, the efficiency of the engine is a critical factor affecting the choice of the fuel source. In the near term, for example, power cogeneration could become an important market in response to the higher cost of electricity during peak demand periods. In the far future, the clean burning characteristics of natural gas may make it the most desirable fuel for advanced, high temperature, high efficiency engines. In both cases, the question of efficiency requires a clear resolution of tribological issues, with the most urgent attention being focused on the unique conditions pertaining to gas-fired prime mover environments.
Results	A critical assessment of the current state-of-the-art of the tribology of ceramics is made. While there are many research issues related to the general application of ceramics in machinery, wear parts, bearings, biomaterials, and liquid-fueled heat engines, there are unique research needs specific to the gas industry. In particular, advanced heat engines designed specifically for gas burning used in energy generation and transportation offer exciting prospects as well as difficult challenges in materials selection, testing, design guidelines, and life predictions.
	The development of the technology for high efficiency gas-burning prime movers is deemed necessary to maintain current and projected utilization levels of natural gas. Further, problems associated with high temperature lubrication of liquid-fueled heat engines, in terms of dispersing soot particulars and the neutralization of sulfuric acidic species (derived from sulfur compounds in

liquid fuels), may delay or prevent the commercialization of high efficiency liquid-fueled adiabatic engines,. Consequently, the clean burning characteristics of natural gas may offer a unique opportunity to capitalize on this market.

Current tribology research efforts on ceramics are plagued by inconsistent methodology, lack of materials characterization, lack of environmental control, and nonuniform sample cleaning and preparation procedures. These practices yield contradictory data and make generalizations of friction and wear characteristics of materials impossible. The ever changing processing techniques for ceramic materials add further measures of confusion. Design guidelines and materials selection become crucial issues. Wear life is controlled by effective lubrication, but lubrication of ceramic materials currently is not understood. Hence, there is no effective lubricant presently available for ceramics at high temperatures. Effective lubrication is also controlled by environmental factors. The influence of gas combustion products on lubricants and ceramic surfaces, therefore, becomes a key focus for GRI.

Based on this assessment, it is recommended that GRI accelerate research in: (1) ceramic materials selection guide for optimum wear life under gas-burning conditions; (2) lubrication research in defining the chemistry, materials, and additives that will function under high temperature gas-burning conditions; and (3) effects of microstructure on wear resistance, surface reactivity, and lubrication requirements under gas combustion environments.

While there is a large parallel effort in developing liquid-fueled heat engines, and while many problems identical in form emerge, it is not clear that solutions that may be derived from liquid-fueled heat engine research can be utilized readily for gas-fired prime movers. The very nature of tribology is governed by systems (speed, load, geometry temperatures, pressures, and lubrication) and environments (combustion gases, contaminants, oxidation, corrosion, and competing processes). Therefore, solutions specific to GRI's needs may not be available from other sources that are not gas related. Results from projects such as materials development, however, can provide useful leads, but even these results must be tested under specific gas-fired prime mover conditions to establish their utility to the gas industry.

Prompt implementation of the research in the recommended areas will not only ensure GRI's position on parallel technology development, but also may provide a unique opportunity to exploit to the fullest advanced technologies for increased utilization of natural gas.

Technical Approach

A review of the tribological issues in engine technology was conducted with an emphasis on the technical barriers confronting the utilization of advanced gas-fired engines. The scope of the study was centered specifically on the tribology of materials in gas fired engine applications. The resulting assessment project probed several sources of fired prime mover technology. The study included discussions of work in progress, site visits, and reviews of open literature. Strong evidence was found during the course of this study to suggest that tribology research will have a major role to perform in the establishment of competitively efficient gas-fired heat engines.

Project Implications

This report is responsive to part of the mandate of the Center for Advanced Materials at The Pennsylvania State University and was funded as a subcontract within the GRI support for that Center.

The Center for Advanced Materials contains a major organizational unit within which material specific aspects of industrial end use technologies based on the actual or potential use of natural gas are assessed in order to define and focus subsequent advanced materials research and development activities at the CAM. The ultimate purpose of such research activity, and hence the objective of the assessment activity, is the maintenance of a competitive position for natural gas among the various sources of energy in industrial end use technologies.

This report covers the area of tribology (i.e. lubrication, friction, and wear of moving parts) with an emphasis on natural gas engines. The technical problems actually and/or expected to be associated with such engines are described, the research state-of-the-art is described, and research needs are outlined. Recommendations for research projects and the implications which the success of such research would have for the natural gas industry are described. Based on this report, research on tribology has been given a priority rating within the general context of research on advanced materials for natural gas applications. Furthermore, the prioritization of particular tribological problems in such applications can now be made.

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ABSTRACT

A critical assessment of the current state-of-the-art of the tribology of ceramics is made. While there are many tribological research issues related to the general application of ceramics in machinery, wear parts, bearings, biomaterials, and liquid-fueled heat engines, there are unique research needs specific to the gas industry. In particular, advanced heat engines designed specifically for gas burning used in energy generation and transportation offer exciting prospects as well as difficult challenges in materials selection, testing, design guidelines, and life predictions.

The development of the technology for high efficiency gas-burning prime movers is deemed necessary to maintain current and projected utilization levels of natural gas. Further, problems associated with high temperature lubrication of liquid-fueled heat engines, in terms of dispersing soot particulates and the neutralization of sulfuric acidic species (derived from sulfur compounds in liquid fuels), may delay or prevent the commercialization of high efficiency liquid-fueled adiabatic engines. Consequently, the clean burning characteristics of natural gas may offer a unique opportunity to capitalize on this market.

Current tribology research efforts on ceramics are plagued by inconsistent methodology, lack of materials characterization, lack of environmental control, and nonuniform sample cleaning and preparation procedures. These practices yield contradictory data and make generalizations of friction and wear characteristics of materials impossible. The ever changing processing techniques for ceramic materials add further measures of confusion. Design guidelines and materials selection become the crucial issues. Wear life is controlled by effective lubrication, but lubrication of ceramic materials currently is not understood. Hence, there is no effective lubricant presently available for ceramics at high temperatures. Effective lubrication is also controlled by environmental factors. The influence of gas combustion products on lubricants and ceramic surfaces, therefore, becomes the key focus for GRI.

To identify the critical technical barriers confronting the utilization of advanced gas-fired engines, data were gathered specifically on the tribology of materials for gas-fired engine applications. Site visits and discussions with a number of GRI contractors in industry were conducted as the first step in identifying critical issues. Then, an extensive review of the technical literature was made to determine what information was available to resolve those issues, and, more importantly, what critical information was not yet available. These data were used to examine the issues for each of the principal engine types (rotary, reciprocating, and turbine). Materials property data for ceramics were then reviewed in the context of the operating environments and conditions for these engines. Thermal, mechanical, and tribological properties were examined along with the important considerations for lubricating ceramics in engine applications. The analysis of these data considered the impact and relative merits of using various advanced materials and resulted in recommendations for research activities that could have a significant impact on the development of gas-fired prime movers.

Based on this assessment, it is recommended that GRI accelerate research in: (1) ceramic materials selection guides for optimum wear life under gas-burning conditions; (2) lubrication research in defining the chemistry, materials, and additives that will function under high temperature gas-burning conditions; and (3) effects of microstructure on wear resistance, surface reactivity, and lubrication requirements under gas combustion environments.

While there is a large parallel effort in developing liquid-fueled heat engines, and while many problems identical in form emerge, it is not clear that solutions that may be derived from liquid-fueled heat engine research can be utilized readily for gas-fired prime movers. The very nature of tribology is governed by systems (speed, load, geometry, temperatures, pressures, and lubrication) and environments (combustion gases, contaminants, oxidation, corrosion, and competing processes). Therefore, solutions specific to GRI's needs may not be available from other sources that are not gas related. Results from projects such as materials development, however, can provide useful leads, but even these results must be tested under specific gas-fired prime mover conditions to establish their utility to the gas industry.

Prompt implementation of the research in the recommended areas will not only ensure GRI's position in parallel technology development, but also may provide a unique opportunity to exploit to the fullest advanced technologies for increased utilization of natural gas.

I. INTRODUCTION

The Center for Advanced Materials was established, in part, in recognition of the need for technical advances in materials science and engineering to sustain, develop, and promote applications of natural gas fuels. As with any new effort, a certain number of cursory studies were required to determine more clearly what the detailed scope of the effort should be. One of those studies was the work reported here assessing the research needs with respect to the tribological aspects of gas-fired prime movers.

This topic was of special interest because the future commercial success of such prime movers may depend critically on the ability of the engines to operate for long periods of time with low maintenance. For example, operation of an engine for 20,000 hours would be roughly equivalent to driving an automobile for 1,000,000 miles at 50 miles per hour. Preventing component wear and failure would be vital to such a fete.

The intent of this tribology study was to provide a brief look at the issues, needs, and priorities for tribology research in gas-fired applications as perceived by current GRI contractors. Discussions with GRI contractors soon revealed that there was a broad-based recognition of the importance of tribology. However, there was no previous review of the tribology of advanced materials focused on gas-fueled applications on which this effort could build. Consequently, the investigators took the liberty of pursuing this study in far greater detail than was requested for the project. An extensive review of the literature was conducted during which a considerable amount of data was extracted to illustrate the current status of the tribologically relevant technical information. Further, these data were used to identify critical research concerns. Recommendations for research on advanced ceramics were developed as a synthesis of the research needs expressed by the GRI contractors and as identified in the data analysis.

Research in tribology provides a basis for the much needed advances in technology that will enable more reliable, efficient, and, therefore, more competitive utilization of natural gas in residential heat pumps, power cogenerators for hospitals and hotels, and engines for transport vehicles.[1-3] Such applications inevitably involve moving parts that cause friction and wear which diminish the reliability, efficiency, and effectiveness of the engine. In these applications, conversion energy is lost from the work done against friction. Perhaps more importantly, parts that suffer wear can cause energy losses due to leakage and can result in premature component failure and, hence, system downtime.

The importance of tribology to efficient use of energy is well recognized.[4-5] More importantly, research in tribology is beginning to be recognized as an essential prerequisite to advances in technological concepts quite generally. For example, in the mid-1980's, several reviews of the need and impact of tribology research were conducted for the Energy Conversion and Utilization Technology program of the Department of Energy (DOE/ECUT).[6] An "Assessment of Government Tribology Programs" found that there were approximately 215 projects being conducted under the sponsorship of 21 government organizations. Most of that work pertained to the Department of Defense, and it was noted particularly that industrial tribology areas received little attention. According to that assessment, past research efforts in tribology had been evolutionary in nature rather than exploratory. However, through such efforts as the assessment, the need for planned, exploratory research in tribology was beginning to be understood. That assessment reported that there were developing efforts in wear research, high temperature lubrication, and ceramic friction and wear. However, it noted that little attention had yet been given to design predictability or to composite materials. It was noted that much of the research concerned lubrication, including efforts to find a synthetic oil to be used in gas turbine engines at temperatures up to 315°C (600°F). Other major efforts were directed towards materials for high-speed rolling contact bearings.

At approximately the same time, an "Assessment of Industrial Attitudes Toward Generic Research Needs in Tribology" also was conducted for the DOE/ECUT.[7] That assessment found that funding for generic tribology research was very limited. Further, when industries did provide funding for such research, there was no focusing of the efforts or coordination of the programs. Generally, expenditures were for the development of specific products. However, discussions with the 27 industries reviewed consistently indicated a need for tribology research results. Technically sophisticated organizations generally expressed a greater emphasis on understanding tribological mechanisms. Four research areas were given special mention. First, there was a strongly expressed consensus that research results were not readily accessible to the potential users in industry. The common methods of reporting research results, such as technical papers and handbooks, were considered to be too limited. Second, there was a broad interest in relating laboratory tests to applications in the field. Third, a growing interest was found in using ceramics in power plants and for specific components such as cam followers, bearings, and cylinder liners. Overall, the assessment concluded that much more data would be needed before applications of engineering ceramics would become generally viable. The fourth area with special emphasis concerned the link between chemical environment and tribological phenomena. The latter issue was noted as the most persistently cited concern in the assessment.

Two other assessments focusing on specific industries and their energy losses that could be prevented or reduced through appropriate tribology research were also made for DOE/ECUT. One of those assessments reviewed industries in mining, agriculture, primary metals, chemicals and refining, food, and pulp and paper.[8] The other assessment reviewed the transportation and electric utilities industries.[9] The latter review examined wear issues and made recommendations for long-term research and development programs. Reliability was considered to be the central theme for research in the utilities industry. General areas of recommended research included component failure analysis, wear rate data, tribology of ceramics, and reliability or durability. Specific problem areas included piston rings, main and connecting rods, bearings, valve trains, oil pumps, abradable seals, and rotor systems.

None of the tribology assessments considered the needs and interests of the natural gas industry except in a cursory manner. Hence, the present assessment effort began with an overview of gas applications in which tribology research could play an important role.

Currently, small, but well established, markets exist for gas-fired reciprocating engines. The oil, gas, and agricultural industries use such engines to provide power for drilling operations, air compression, and fluid pumping. In these applications, the local availability of natural gas as a fuel may be a bigger factor than efficiency in the decision to use gas-fueled engine. In contrast, gas-fired turbine engines are widely used in power plants. In these gas turbines, reliability, lifetime, and maintenance interval can be more important considerations than efficiency. However, in future potential markets, high efficiency in energy conversion could become a more critical issue. As the energy usage increases, power cogeneration could become an important market for natural gas in response to the higher cost of electricity during peak demand periods. The clean burning characteristics of natural gas may make it the most desirable fuel for the more advanced, high temperature, high efficiency adiabatic engines, resulting in another potential market for natural gas. In both of these applications, the increased need for efficiency requires a clear resolution of tribological issues, with the most urgent attention being focused on the unique conditions pertaining to gas-fired prime mover environments.

In general, the consequences of putting two material surfaces into contact under relative motion depend on many complex and interdependent variables. Viewed microscopically, the surfaces of the materials, even when highly polished, have numerous irregular topographical features called asperities. During contact, the loading of one surface pressing against the other is actually supported by these asperities. Since the surface area of the asperities is usually quite small, the stress developed in an asperity can be very large, approaching the yield strength of the material. When the two surfaces are in relative motion, additional sever straining occurs when the asperities of one surface collide with the asperities of the other surface. The asperities may suffer plastic deformations, crack generation, fracture, or phase transformations as a result of the collisions. There is evidence that very high temperatures, on the order of 1500 - 2000°C, are also associated with asperity-asperity collisions. The effects of the localized temperature extremes on the tribological performance properties of the materials are not known at this time. It may be conjectured, though, that asperity-asperity collisions are a critical part of the wear process.

As a result, the variables that are important to the tribological aspects of engine operation include speed, load, geometry, temperature, materials, pressure, and the specific conditions associated with the operation of the system, such as atmosphere, contaminants, wear history, and surface compositional changes.

Tribology involves nonequilibrium, nonlinear, nonsteady state, dynamic processes and interactions of materials that depend not only on <u>what</u> materials are used, but also on <u>how</u> the materials are used. In other words, to design a tribological system properly, the dependencies of performance on the total system being investigated must be considered, particularly the roles of the materials, the lubricant, the environment, and the operating conditions. Consequently, the tribological characteristics encountered in the use of advanced ceramics in gas-fired prime movers will have features distinct from the characteristics encountered in studies of liquid-fueled engines. The consequences of using natural gas as a fuel have not been studied previously.[10-14] The only way to verify and to understand the significance of those tribological features specific to gas-fired environments is to conduct experiments specifically designed to examine advanced ceramics in gas-fired environments.

Natural gas consists essentially of methane gas. Methane burns more cleanly in air than do gasoline or diesel fuel. The combustion products of natural gas are mostly CO, CO_2, and NO_x. These products are rather different from the products of liquid fuel combustion. As a result, the interactions among the engine surfaces, the combustion products, and the lubricant for future gas-fired heat engines may be quite different than for the future liquid-fueled heat engines. Also, certain mechanical aspects of the combustion process will be different when gas is used as a fuel and need to be considered. For example, methane gas is found to explode in an uncontrolled manner when it is used at high compression ratios (approximately 15:1) such as are used in a diesel engine. To prevent that situation, the diesel engine design may have to be modified for gas fuel to make use of a lower compression ratio (approximately 10:1). However, at this lower compression ratio, spark ignition is required along with a carbureted fuel system. Unfortunately, the end result of such an adaptation would be an engine that produces only about 75% of the output power of the unmodified diesel engine.[15-16]

In principle, increasing the compression ratio towards 15:1 would increase the efficiency and power output of the gas-fired engine. To do so, however, methods to overcome or eliminate the uncontrolled detonation of the natural gas fuel mixture must be found. Two different approaches to this objective are under consideration in GRI supported research. The first method is simply to reduce the amount of gas in the fuel and air mixture. The resulting lean burn condition, however, necessitates further design modifications such as a precombustion chamber and/or a more turbulent main combustion chamber. It is anticipated that the lean burn approach could lead to an engine efficiency on the order of 33%. This efficiency would still be significantly less than the 37% rating achievable by diesel engine designs.

The second approach to increasing the compression ratio is to eliminate the fuel-air mixture detonation problem completely by using a direct fuel injection technique. Again, engine modifications would be necessary to provide both an injection mechanism and an appropriate ignition source. The important advantage in using direct injection of the gas fuel is that the constraints imposed by the detonation problem would be removed. Hence, the compression ratio could be higher, and, perhaps more importantly, the temperature of the combustion chamber could be increased significantly. The latter advantage would require the use of insulating materials such as advanced ceramics for critical engine components. The resulting engine could achieve a maximum efficiency of 38-40%.

From these considerations, proper tribological treatment may be needed with respect to materials selection and the lubrication of the components in the various engines. Therefore, a critical review of the status of the tribological issues in engine technology has been conducted to identify the technical barriers confronting the advanced utilization of gas-fired engines. The scope of this study is centered specifically on the tribology of materials in gas-fired engine applications.

II. OVERVIEW

Wear and lubrication problems currently exist for all high temperature, high efficiency heat engine critical moving parts, particularly seals, piston and cylinder contacts, apex-housing wear in rotary engines, and valves, valve seats, and valve stems. Ceramics are materials of choice due to their high temperature strength and wear resistance. Unfortunately, the wear rates of ceramics are very high causing premature failures. It is not clear whether the high wear rate is attributable to materials inadequacy or to lack of effective lubrication. Very little definitive data exist. Such data, essential to design criteria, must be acquired through system specific research efforts.

Such conclusions were derived from an analysis of information available in technical literature and from visits and discussions with industries and research groups involved in GRI-supported or related engine research. Site visits provided the most important source of relevant information in terms of focusing on the immediate problems, understanding the current attempts to resolve the problems, and gaining an insight on the nature of the research needed to obtain longer-term solutions capable of advancing high efficiency engine technology. While many companies and individuals were contacted, research groups at Caterpillar Tractor Co., John Deere Co., and Southwest Research Institute (SwRI) proved to be the most helpful and GRI specific.

The visit to SwRI was particularly fruitful. Discussions indicated a primary concern with three problem areas. In the wear of engine components, the immediate problem with piston-type engines was considered to be the wear of the valve and valve seat assembly and the valve stem. It was felt that the mechanical designing of a more efficient engine had been accomplished, but that the associated materials problem had not yet been solved. The difficulty was that the more efficient engine operated at higher temperatures. For significant increases in efficiency, the temperature increase was large enough to make the use of metal alloys less appropriate. The most promising solution to the problem, especially for long-term results, was expected to be obtained through the use of advanced ceramic materials. A related problem, lubrication at the higher temperatures, was also considered to be essential to the progress in engine technology. The technical basis for developing new lubricants for higher temperatures and/or for ceramics has not yet been established. Substantial and comprehensive data on the stability of lubricants, the effectiveness of controlling wear and friction at high temperatures, and the tribological properties of ceramic materials were much needed. SwRI also emphasized the need to relate such data to engine conditions, laboratory bench tests, and engine test rigs. Interest was expressed particularly for wear models that could be used to extrapolate wear rates obtained in rig tests for 2000 hours to full scale applications of 20,000 hours.

The group at Caterpillar Tractor Co. indicated that they considered two problem areas to be especially important: lubrication of advanced engines and valve wear. In advanced engine designs, lubricant consumption and the formation of deposits were highlighted as the major problems confronting current and near future efforts. It was emphasized that lubrication was the key limiting factor in the development of a low heat rejection engine. A need for laboratory tests correlated to engine tests was also strongly indicated. Special problems in lubrication and wear were discussed for the use of natural gas as a fuel. The combustion products of natural gas are relatively dry when compared to gasoline or diesel fuels. The cleaner natural gas, while highly desirable, creates a greater reliance on the effectiveness of the lubricant in preventing engine failure. Further, the environmental effects on the wear process are not adequately understood. For example, upon changing to a lean burn condition, valve wear was seriously increased. The need for materials related research, centered most likely on ceramics, was indicated as a high priority.

The John Deere facility at Woodbridge, New Jersey and Moline, Illinois were also visited. The focus of the discussions was on a high efficiency rotary engine as a gas-fired prime mover. The design of the rotary engine is simple in principle and has specific advantages resulting from fewer moving parts. However, the apex seal is crucial to engine operation. Hence, the wear of the apex seal/rotary housing couple is an immediate and a long-term concern. Wear of the apex/housing couple creates a leakage that results in a reduction of power output and efficiency. Such leakage can also contribute to the formation of deposits on the surface against which the apex seal must slide. These deposits become traps for wear debris and also create nonuniform surface profiles resulting in further wear. Such deposits can also occur directly prior to significant leakage at the apex seal and thereby contribute to accelerated wear. Advances in rotary engine development, therefore, are hindered by two distinct tribological problems: wear of the rotor apex/housing couple and the formation of degraded lubricant deposits. Solutions to these issues, however, are interconnected. Under the design conditions, the materials used may not be adequate. At the same time, the materials may be inadequate because of the lack of adequate lubrication. When a satisfactory lubricant is available, the materials may be sufficient. To safeguard technology development, a dual approach seems appropriate; i.e., a parallel development effort of materials and lubricants. Efforts in defining a more durable metal alloy or a surface modification treatment may provide a short-term solution. However, in the context of using the rotary engine in cogeneration applications, the need for significantly increased efficiency may dictate that advanced structural ceramics be used.

A persistent theme in the discussions with various engine research groups was the need for new materials for which advanced ceramics were considered to be the leading candidates. Independent analysis of the materials criteria for advanced engine designs leads to the same conclusion. Given the goal of higher efficiency, in the range of 37-40 percent, it has become clear that the waste heat energy must be reduced. Approximately one-third of the energy developed in combustion is lost in nonrecoverable form by diffusion through the engine parts. While unrecoverable, such losses are preventable by using improved thermal insulation. In principle, then, increasing the efficiency of the engine is rather straightforward. However, increasing efficiency while simultaneously maintaining adequate wearlife and system reliability is a far more complicated matter. Overall, the materials requirements for advances in heat engine technology require reductions in heat loss, high wear resistance, low friction, reduced lubricant deposits, and, in some cases, less engine dead weight or inertia. The only materials that currently have the potential of satisfying all of these requirements are advanced structural ceramics.

Discussions with engine research groups, analysis of engine materials requirements, and a review of current literature on engine research strongly suggested the need for a critical assessment of ceramic tribology. A major review of the technical literature was conducted to learn what information was available on the wear of ceramics under any conditions. A computer search of the literature covering the time period from 1955 to the present was performed. Approximately 1200 articles were found pertaining to the wear of ceramics, with an emphasis on the wear of specific ceramics (silicon nitride, silicon carbide, alumina, and partially stabilized zirconia). These papers were further screened by requiring that the data in the papers be susceptible to critical evaluation; i.e., enough information had to be contained in the paper such that data from different papers could be compared in common terms. For example, comparisons of the wear of a material as a function of load and sliding speed could be accomplished only if the dimensionless wear coefficient could be computed, the sliding speed could be determined in a common unit such as meters per second, and the load could be expressed as the normal load. Applying this requirement reduced the number of papers to be reviewed to seventy. Thus, the first conclusion found in the literature review was that comparisons of data from different studies is a major problem in the current data base.

The review then proceeded along two paths: What materials data were available on ceramic materials for gas-fired prime movers? What tribological data existed on ceramics for advanced heat engine technology? Implicit in both paths was the question, "what data are missing?"

Data gathered from the site visits, the literature review, and other contacts and discussions are analyzed in the following sections. The section on Issues concentrates on each type of gas-fired prime mover and cogeneration engine with an emphasis on applications, advantages, and challenges. The section on Materials Analysis considers the impact and relative merits of various advanced materials. Section IV reviews the status of the Tribology of Ceramics with respect to critical considerations for heat engines. Section V analyzes the lubrication requirements of ceramics. The final section, Recommendations, discusses the research activities which could have a significant impact on the development of gas-fired prime movers.

III. ISSUES

Potential applications of gas-fired prime movers exist for each of the principal engine types (reciprocating, rotary, and turbine). The operating conditions and the demands placed on the engines vary significantly with the intended application and engine design.

The critical issues are: efficiency, reliability, lifetime, and cost. Each of these factors is directly linked to tribology. For example, wear is the controlling parameter for reliability and lifetime. Friction governs efficiency. The cost can be heavily influenced by friction and wear characteristics of materials, the materials costs, and the durability of the materials.

Each engine type is discussed separately. The nature of the engine, the intended and potential applications, and the operating conditions and demands placed on the engine are reviewed first to establish the context and scope of the research areas. Next, special problem areas perceived as major barriers to advances and developments in engine technology are discussed with an emphasis on those problems requiring concurrent advances in fundamental material and lubrication aspects of tribology. Each subsection concludes with a discussion of the generic material properties that will be needed to advance the engine design. In each case, materials currently considered as the leading candidates to fulfill the material requirements are identified.

A. Rotary Engines[17-27]

The rotary engine is the simplest mechanical form of the engine designs in terms of its small number of moving parts. A schematic rendering of its operation is given in Fig. 1. The heart of the engine is the triangular rotor that rotates within a trochoid surface at operating speeds that range from a few thousand to as high as 11,000 rpm. Each face of the rotor functions as a combustion chamber. The combustion cycle begins when an apex seal uncovers the air intake port allowing air to enter the immediate chamber. When the next apex seal closes the intake port, compression of the air begins. A fuel charge is ignited in the chamber at the point of maximum compression of the air (compression ratios in the range 7 to 10). In the resulting power stroke, the apex seal uncovers the exhaust port allowing the gases to exit the chamber. During this operation, the apex seals may experience temperatures of the order to 500°C.

The small size, low vibration, and potentially low maintenance make the rotary design suitable to a number of lower power domestic applications such as heat pumps and stationary power cogeneration functions. The high power density and high speed capabilities give the rotary engine significant potential for high power transport applications. Consequently, designs for the rotary engine range from a few kilowatts of power output to 1700 kW.

The major problem areas of the rotary engine are the wear and lubrication of the rubbing surfaces. Wear of the apex seal, for example, causes leakage that results in higher fuel consumption and reduced power output. Wear also occurs on the trochoid surface, the side housing, and at the corner and oil seals. Elimination of these losses could contribute as much as ten percent improvement in both fuel consumption and power. For the smaller size engines, the overall efficiency of the engine must be improved to be competitive with existing alternative designs. Improvements due to reduced leakage losses, while important, would not be sufficient to make the rotary engine highly attractive. Other efforts to reduce losses such as by improved insulation of components are highly desirable. Improved heat insulation, though, places greater demands on the material characteristics and makes the tribological conditions more severe. In general, the ideal materials would have low wear and low friction to ensure durability and mechanical efficiency, but also would have to possess low thermal conductivity, high temperature strength, high fracture toughness, and good thermal shock resistance.

Currently, the approach taken by the industry to secure improved performance for the rotary engine is to seek surface coatings or modified surfaces that are harder and more wear resistant than the steel substrate material. Special heating and rapid solidification techniques are being applied to produce a modified surface layer on the contacting surfaces. The method produces a thick surface layer (about 3 mm) that has reduced friction. Other surfaces are being hardened through chromium plating and soft nitriding. Special coatings of tungsten carbide and chromium oxides are also being used to improve surface wear resistance.

More advanced approaches are attempting to utilize the inherent thermally insulative properties of high technology structural ceramics. Monolithic ceramics made from silicon nitride, silicon carbide, and partially stabilized zirconia (PSZ) are the leading candidate materials. Ceramic coatings using chromium oxide over PSZ is considered to be another possible useful approach that combines the thermal characteristics of PSZ and the wear resistance of Cr_2O_3.

Successful application of these new materials hinges on the development and availability of effective lubricants for these materials. Detailed discussions are presented in section V.

B. Gas-Fired Reciprocating Engines[28-29]

Reciprocating engines are the most widely used type of engine currently produced. Hence, there is a wealth of industrial experience in the design and operation of such engines that may be called upon in the development of gas-fired piston engines. There are several reasons to suppose that such engines would have a useful and viable position in the commercial marketplace. Natural gas burns more cleanly than either gasoline or diesel fuels. As a result, one would expect fewer maintenance problems arising from deposits and corrosion. The lifetime of a gas-fired piston engine should, therefore, exceed that obtained from liquid fuels.

The basic operation of the piston engine involves several moving parts for which tribological considerations are crucial, as suggested by Fig.2. Valves control the intake of the air and gas and the exiting of the exhaust. The combustion chamber is defined by the cylinder head and liner components and the top cap of the piston. Air and fuel enter the chamber as the piston recedes from the cylinder head. The valves are closed during the subsequent compression stroke which continues until a compression ratio is achieved in the range from eight to fourteen. The fuel and air mixture is ignited at the point of maximum compression to begin the power stroke. The cycle is completed by the exhaust stroke.

Gas-fired reciprocating engines are being developed for stationary applications such as residential heat pumps and large size power cogeneration units for use in hospitals, hotel, and other facilities. The power capabilities needed for such engines range from a few kilowatts to over 500 kW. The central issue that needs to be addressed by the engine developers pertains to the efficiency of the engine compared to existing alternate designs. The current thermal efficiency of approximately 30% must be improved to the 40% range to make gas-fired piston engines competitive. To achieve such improvements, it will be necessary to utilize new materials such as high technology ceramics.

The efficiency and durability of the piston engine is strongly related to the wear life and friction characteristics of the components that encounter sliding wear. The cylinder liner, piston rings, valves, valve seats, and valve stems, in particular, may contribute to wear related problems. The valve and valve seat may also experience impact wear. To improve the efficiency of the engine, these parts need to have improved thermal insulation such that heat losses through various cooling mechanisms can be reduced. Efficiency could also be improved through the use of lighter weight materials. The need for better insulation, higher temperature capability, and lighter weight again suggests the use of ceramics. Silicon nitride is the leading material, but use of this material requires a suitable mating surface for which there would be relatively low wear and friction. A major difficulty in the developmental area is the lack of basic data on the wear of ceramic pairs and materials compatibility.

C. Low Heat Rejection Diesel Engines[30-35]

Advances in the design of diesel engines currently are focusing on the development of low heat rejection (LHR) engines, sometimes also called adiabatic diesel engines. These engines are intended for use in heavy duty transport applications and would not generally be expected to consider natural gas as an appropriate fuel. However, the experience gained from the research on materials for LHR engines could be valuable to the development of gas-fired engines. Indeed, the most advanced research efforts on the use of ceramics and other state-of-the-art materials have been made for LHR diesel engines.

The tribological problem areas for LHR diesel engines, in fact, are essentially the same as those for gas-fired piston engines: cylinder liners, piston rings, valves, valve seals, and valve stems. The primary difference between these engines is that LHR diesel engines are being designed with much higher operating temperatures. The near-future goal is operation at 600°C, while in the far-future temperatures may reach 1000°C. The material needs for the LHR engine at 600°C, in terms of the thermal characteristics, should be expected to be similar to the material needs of the rotary apex seal at 500°C.

The emphasis in the design of the LHR diesel engine is to eliminate, as much as possible, the loss of energy to cooling. Such losses amount to approximately one-third of the heat energy released in the combustion process. Within the combustion chamber, the heat energy impinges directly on the cylinder liner, the piston cap and rings, the cylinder head, and the valve assembly. These components, therefore, must have a high thermal shock resistance as well as excellent friction and wear resistance. These components also interface with other engine parts that are at much lower temperatures. Hence, monolithic high temperature components need to have good dimensional stability in the presence of large temperature gradients. If thermally insulating coatings are used instead of monolithic materials, then the thermal expansion coefficient of the coating material needs to be compatible with the thermal characteristics of the substrate. The materials meeting these requirements are the advanced structural ceramics. The leading materials in current research efforts are silicon nitride and silicon carbide. Coating materials of titanium carbide, chrome plating, and chromium carbide are also being considered.

The most frequently cited barrier to the development of the applications of ceramic materials results from the lack of comprehensive understanding of the performance properties of structural ceramics. Basic data are needed in every aspect of characterization of the material, mechanical and material properties, and tribological performance results. In the latter area, wear, friction, corrosion, and deposit formations need to be understood in the context of the operating environment of the engine. In particular, the tribology of ceramic materials at high temperature and reaction chemistry at high temperature need significant advances, beginning with the development of a comprehensive data base.

D. Turbine Engines[36-37]

Gas-powered turbine engines are currently well established as high power industrial cogenerators with power levels ranging from 500 kW to 100,000 kW. In these applications, gas turbines are particularly noteworthy for their high degree of reliability. This reliability factor is significant in terms of both servicing considerations and overall operating economics. Higher reliability corresponds to lower maintenance costs, longer lifetimes, and less loss of production time due to unscheduled downtime. These engines also have a relatively high operating efficiency and a low pollution output. The advantage of higher efficiency, however, does not persist to lower power levels. Currently, a gas turbine engine operating at low power achieves an efficiency of only about thirty percent. For potential applications in the 50-100 kW range, the efficiency would have to be improved to the 40% level to be cost competitive with other engine types.

The primary near future possibility for improving the efficiency of gas turbine engines is to increase the turbine inlet temperature which may be achieved by using advanced structural ceramics. The basic material requirements to be considered, low weight density, good thermal insulation, and high thermal shock resistance, are characteristics for which ceramics are widely noted.

IV. MATERIALS ANALYSIS[38-65]

Successful development of competitive gas-fired engines for cogeneration and transport applications may be achievable through the use of ceramic materials for critical components. In its most rudimentary context, the successful development of these engines will be determined by only one factor: cost. That factor, however, is a function of three technical considerations: efficiency, lifetime, and reliability, as well as the direct economic considerations in the procurement of materials and fabricated components. The three engine performance variables can be enhanced by using ceramic materials in the engines, provided such materials achieve reductions in:

a. Heat loss
b. Dead weight and inertia
c. Wear
d. Friction
e. Deposits

Each of these factors will vary with the material that is selected. The thermal and tribological factors will depend further on the temperature and other environmental conditions under which the material components must operate. In general, the desirable properties of the materials used in gas-fired engines may be summarized as in Table I. These properties may be organized into a somewhat logical order by considering the relative necessity of each property. Thus, for example, the fact that the material must maintain its structural integrity at the operating temperatures experienced by the components requires that the material not melt or undergo any other change of phase at any temperature up to the operating temperature. Consideration of the potential temperature levels that could be generated by asperity-asperity collisions also suggests that having a very high melting point might be desirable. Even supposing the existence of a structural material that maintains its structural integrity at high temperature, it must also have relatively good insulating properties such that the heat loss can be reduced. Use of such a material in an engine environment requires that its mechanical strength be sufficient for the application as a structural component. In operation, it is vital that the material not experience such wear that the power level is reduced or that engine failure is accelerated. Furthermore, the material itself should not create a load that diminishes the useful power output. Thus, the coefficient of friction should be minimized and the density of the material should be as low as feasible. The material must be capable of cycling through a wide range of temperatures to permit servicing and engine shutdown. Hence, the material should have a high thermal shock resistance. For coatings and for monolithic components that have an interface with a metal part, compatibility of the thermal expansion characteristics will be needed. Dimensional stability may also be an important consideration over a wide range of temperature.

Among current materials, various grades of silicon nitride, silicon carbide, and zirconia are being given the most serious consideration for use in gas-fired engines. Figures 3-12 compare these materials in terms of the properties most desired for engine applications.

The melting points or decomposition temperatures (T_M) shown in Fig. 3 for the primary candidate materials are all relatively high in temperature compared to the anticipated operating conditions. However, in a tribocontact, collisions between surface asperities can result in much higher local temperatures. Indeed, compared to the potential asperity-asperity contact temperatures (T_A = 1500-2000°C), the decomposition temperature for silicon nitride may be considered marginal. The consequences of an asperity-asperity contact temperature being approximately the same as the melting point or the decomposition temperature are not known experimentally, but it may be speculated that there are both beneficial and harmful effects. If entire surface layers of a material were to melt or merely soften, accelerated wear rates would be expected. When such softening or melting is restricted to micro-regions, the localized wear rate may increase. Alternatively, it is conceivable that such localized micro-melting would produce a beneficial effect in the form of regional lubrication. Glassy disordered surfaces that have been observed in some wear tests of ceramic materials might have been the result of such micro-melting processes. Thus, if $T_M = T_A$ is desirable, then silicon nitride might be the material of choice. However, if $T_M >> T_A$ is more important, then the choice would be between silicon carbide and a zirconia material. A preference might be given to silicon carbide because of the harm that might result from using unstabilized zirconia at temperatures near its high temperature crystallographic phase transition.

The primary contribution to increased efficiency introduced by the use of ceramics results from their capacity to reduce heat losses. The diffusion of heat through a continuum solid depends on the thermal conductivity (K) and heat capacity (C) of the material and the bulk density (ρ) of the substance. The relative influence of each of these factors is summarized by way of the diffusivity ($D = K/\rho C$). The greater the diffusivity, the less effective the material will be in inhibiting the loss of heat energy to coolants. Figs. 4-6 compare the thermal parameters for the principal ceramics. Thermal conductivity has the dominant effect on the transport of heat. It is clear that the zirconia materials with exceptionally low thermal conductivity provide the best thermal insulation. Silicon nitride will transport approximately twice as much heat as zirconia under the same conditions, while silicon carbide transports heat at approximately four times the rate of transport in zirconia.

Use of thermally insulating ceramics will increase the operating temperature of the engine. The material characteristics of ceramics cause further temperature increases at asperity-asperity contacts. Wear rates under these conditions may accelerate as a result of the softening or weakening of the material under the increasing temperature. Consequently, it is important that the material not only be structurally strong, but that it also retains its strength as temperature is increased. Figures 7 and 8 examine these tendencies for the principal ceramics in terms of their flexural strength at room temperature and at 1000°C. Partially stabilized zirconia has the highest flexural strength at room temperature, but the strength rapidly deteriorates at higher temperatures. This property of zirconia may preclude its use in any high efficiency advanced engine. Hot pressed silicon carbide, in contrast, has a relatively high strength at room temperature and retains most of that strength at 1000°C. Hot pressed silicon nitride also shows good strength retention, though it does not do as well as silicon carbide. The remaining grades of materials show much less effectiveness with respect to the retention of strength.

The fracture toughness of the principal ceramics is similar to the flexural strength property in terms of the general performance trend as seen in Fig. 9. Partially stabilized zirconia has a high fracture toughness at room temperature but does not retain that high value at elevated temperatures. Hot pressed silicon nitride performs reasonably well under the fracture tests, as does pressureless sintered silicon nitride. Hot pressed and pressureless sintered silicon carbide are somewhat lower in fracture toughness than silicon nitride, but the retention of performance to higher temperatures is better.

In an engine environment, the ceramic material may be required to cycle through rather wide temperature ranges during operation as well as during start-up and shut-down. The wear rates of the materials may increase under these conditions due to thermal shock effects. Microcracking and crack growth may occur in the surface layers especially where the stress field from the tribocontact is large. High thermal shock resistance, therefore, is desirable for durability and wear resistance. Figure 10 shows that silicon nitride is distinctly better in this characteristic than the other principal ceramic materials. Both pressureless sintered and hot pressed forms of silicon nitride exhibit approximately twice the thermal shock resistance of the other materials and hence, should suffer less deterioration in wear resistance from thermally induced degradation in the microstructure.

Additional potential advantages of using ceramics in heat engines include reduction in weight and increased dimensional stability. Figure 11 shows that the principal ceramics are all relatively light. Silicon nitride and silicon carbide have comparably small densities, while zirconia is nearly twice as heavy as the other materials. For applications requiring minimum weight for optimum efficiency, such as for rotors, the difference between zirconia and silicon nitride or silicon carbide is quite significant. Distinct differences also occur in Fig. 12 for the linear thermal expansion coefficient. Zirconia exhibits a large value for thermal expansion which could be advantageous when the ceramic material must maintain a small differential dimensional tolerance with a metal component. Cast iron, for example, has a thermal expansion coefficient comparable in value to that of zirconia. However, to maintain optimum dimensional stability, silicon nitride would be best. Dimensional stability would be advantageous in maintaining the tolerances of the seals between wearing surfaces.

Use of ceramics under engine operating conditions exposes the materials to reactive environments for long time durations. Oxidation and other reactions with the gas combustion products may alter the material and structural composition of the surface layers of the components significantly. Such reactions therefore also may influence the mechanical and tribological characteristics exhibited by the components. Wear rates and mechanisms and friction are specifically subject to adverse variations. Oxidation reactions in silicon nitride, for example, create an oxide scale of predominantly SiO_2. Alkali impurities in the near-surface bulk material may also migrate along grain boundaries to the surface and form additional oxidation sites. These changes in composition and chemical structure may alter the strength of the material, modify the surface microstructure, or even cause a phase instability in the surface layers. Such effects could produce higher wear and material failure rates. Little applicable data is available for direct use in understanding wear processes in the presence of oxidation. However, static measurements of oxidation resistance can be made and used as an initial indication of the severity of the surface alteration. Such measurements, expressed as percent weight change per hour, show values that range over several orders of magnitude. Silicon nitride materials, for example, have initial values from 3×10^{-5} hr^{-1} to 3×10^{-2} hr^{-1}, while silicon carbide ranges from 10^{-4} hr^{-1} to 10^{-3} hr^{-1}. These values have a very large variation because the oxidation reactions depend strongly on the impurities and sintering aids that may be present, along with microstructural factors such as porosity, pore size, and other effects that vary the reaction surface area. The current data suggest that silicon carbide materials have a greater resistance to oxidation than silicon nitride materials.

Other properties of direct and critical interest to tribological performance and characterization suffer from a sparsity of data. The surface hardness values of ceramics at elevated temperatures, under wearing conditions, and under reactions with the combustion products from the fuel are not well studied. Likewise further data are needed on the creep strength of ceramics, oxidation resistance, reactivity with combustion products, and, of course, detailed data on friction and wear mechanisms.

Based on the information discussed in this section, no one ceramic material can be identified as distinctly superior to the other principal ceramics. However, current zirconia materials may be cited for their more severe limitations and, hence, may be considered to be less likely to be used in engines. Hot pressed silicon nitride and hot pressed silicon carbide have the best characteristics with respect to potential tribological performance. Where high temperature strength is the only, or overriding, consideration, silicon carbide would be the material of choice. However, when overall thermal and mechanical efficiency are important, silicon nitride would be preferred among current ceramics.

In many cases, the selection of a material may be determined, not by the intrinsic materials properties, but by considerations of tribological factors. Early knowledge of the wear, friction, and durability characteristics could avoid the use of materials which are subsequently rejected. Moreover, tribological performance data could provide key information in the optimization of control parameters used for developing a new generation of ceramics for advanced gas-fired engine designs.

V. TRIBOLOGY OF CERAMICS[66-86]

An extensive survey of the technical literature has revealed very little consistency in the manner in which data have been accumulated on the many aspects of the tribology of ceramics. This lack of consistency has been the direct result of the lack of understanding of the full complexity of the problems encountered with ceramic materials. The complexity, though, has gained recognition through several major research efforts initiated quite recently. The Gas Research Institute has established the Center for Advanced Materials at Pennsylvania State University, for which the present assessment was conducted. The Department of Energy has included ceramics as a significant portion of their ECUT/Tribology program. The ASTM has begun the task of developing industry standards for the specification and testing of ceramics. An international effort, VAMAS, has been started to promote international consistency in measurement procedures. And, an interagency government project, sponsored by DOE, NBS, NSF, DOD/Ft.Belvoir, and DOD/Wright-Paterson, has initiated an effort to establish A Computerized Tribology Information System (ACTIS) to greatly enhance the communication and accessibility of tribology data, design codes, and other information of value to U. S. industry.

The lack of consistency among researchers, with respect to measurement techniques, materials characterization, and the specification of test conditions, inhibits the establishment of broad generalizations of trends, correlations, or theories of any significant scope. However, it may be useful to examine a few selected portions of the literature to gain an appreciation of the problems involved. In such an exercise, though, certain caveats must be accepted:

** The designation of a material as silicon nitride or silicon carbide or any other ceramic must be understood to be an approximate material specification of the lowest order. The minor constituents of the test material, which may be sintering aids or other impurities, the nature of the microstructure, the porosity, the grain size distribution, the location of the impurities and defects, and other considerations can have significant effects on the results of friction and wear testing and on the effectiveness of a lubricant.

** The determination of a wear rate may be highly dependent on the measurement technique. Differences in contact geometry, sample sizes and orientations, specimen holder characteristics, and other system variables can result in differences in the dominant wear mechanism and, hence, differences in wear rates.

** The reported friction of a given ceramic pair may depend critically on the presence of unsuspected surface contaminants.

With such caveats in mind, it may be useful to observe selected results on the more central concerns of the tribology of ceramics.

Wear mechanisms: The diversity of results in the current literature is reflected in the diversity of interpretations that have been made concerning the mechanisms of wear. Table II summarizes the principal mechanisms that have been cited as controlling the wear of the four most studied ceramics, alumina, silicon nitride, silicon carbide, and partially stabilized zirconia. In general, the wear of a material may be expected to depend on several classes of variables, including material properties, environmental conditions, and the operating or test configuration. Plastic deformation and fracture often have been considered to be the most prominent factor in the wear of ceramics, but arguments also have been advanced indicating that crack propagation, surface fatigue, and thermally induced stresses may play major roles. Environmental factors have been noted in several papers, primarily in terms of the effects of adsorbed water or humidity. The role of tribochemistry in wear phenomena has become increasingly prominent in the more recent discussions of wear mechanisms, reflecting the growing recognition that many factors are involved interactively in the wear process.

Material variations: Figure 13 illustrates the variation in wear test results that may occur when two nominally equivalent materials are tested in the same apparatus by the same operator under the same external conditions. The figure shows results obtained for two different batches of alumina balls produced by the same manufacturer. The primary differences between the two materials was found to be in the microstructures.

Environmental effects: Figure 14 shows the wear rate of a hot pressed silicon nitride material in air with various conditions of humidity. With increasing humidity, the wear rate could be changed by two orders of magnitude. These results provide a dramatic illustration of the role of tribochemistry in the wear processes of ceramics.

Structure and phase transformations: The structure of a single crystal of a material imposes an orientational dependence on the interaction of molecules at the crystal surfaces. Different faces of a single crystal grain of material present different atomic orbitals for interaction with the contacting tribomaterial and with any lubricant molecules or surface impurities. The resulting surface characteristics may possess an anisotropy that affects the observed wear phenomena. An example of such anisotropic behavior is shown in Figs. 15-16 for alumina.

It must be expected, further, that any change in the structure of the material would affect the wear results also. The phase diagrams of most ceramics exhibit numerous crystallographic structural forms as shown, for example, in Fig. 17 which illustrates the pressure-temperature phase diagram for zirconia. In a tribocontact, both temperature and pressure can vary over a wide range in an extremely short period of time, on the order of nanoseconds. At the extremes of the pressure and temperature excursions, grains of material in the contact may undergo phase transformations which dynamically affect the wear mode of the material. Monoclinic zirconia, for example, has been observed to yield tetragonal zirconia wear debris in some wear tests.

Friction and wear: Studies on the wear of ceramic materials may be found in the literature for a variety of test conditions. Results from those studies can sometimes be compared, as in Figs. 18-22. Such comparisons are obtained by computing the values of the wear coefficients for the respective cases. The wear coefficient is a normalized measure of wear based on the wear volume per unit sliding distance per unit normalized load. The normalized load is the applied load divided by the material hardness. For data comparisons, the wear coefficients may be evaluated if the wear results, details of the test geometry, and material properties are reported. Treating all materials of a given material class, such as alumina, as being equivalent, results ranging over several orders of magnitude are found in each case. Understanding these results and their great variances will be critical to advanced applications of ceramics in heat engines. To gain such understanding, the interaction of the primary variables in the wear process must be investigated in experiments designed to focus on the interactions and their consequences. For example, variation of the operating conditions in a given wear test apparatus can produce dramatic changes, essentially transitions, in both wear rates and friction. Figures 23-25 show such a transition in these performance characteristics for silicon nitride as a function of sliding speed in a pin-on-disk apparatus. It is not clear at the present time whether such transitions are due to the contact temperature increasing with higher sliding speeds; the occurrence of large temperature gradients between the rubbing pair of materials; or due to material fatigue consequences. Figure 25 illustrates the occurrence of wear transitions for a variety of materials as a function of the applied load in a four-ball wear test. Both the location of the transition and the severity of the transition clearly vary with the material. The fact that wear transitions occur at all is a highly significant consideration for designers who intend to use ceramics for engine components that will experience wear. Obviously, the design of such components should be such that the material operates in the lower wear region rather than the higher wear region.

Material durability: Friction and wear transitions can also occur as a result of accumulated damage to a surface that experiences repetitive wear. Figure 26 shows an example of this behavior for silicon nitride. Changes in the surface microstructure due to plastic deformation and crack growth may be especially important in this phenomenon.

Material porosity: The porosity of the ceramic specimen can have a large effect on the measured wear results, as shown in Fig. 27. To some extent, differences in porosity may also reflect other differences in the microstructure and composition since these variations in porosity are produced by changing the processing procedure and the sintering aid chemistry.

Lubrication: Studies on the lubrication of ceramics are all very recent. Data in the literature are very sparse and are essentially restricted to considerations of lubricating materials developed for metals. Conventional lubricants reduce friction and wear of ceramics compared to dry sliding results, but the extent of that reduction and the optimization of the formulations will require a significant research effort. New lubricating materials may be needed, and a fundamental understanding needs to be developed concerning the interactions of the constituents of the lubricant and the atomic or molecular species present on the surfaces of the ceramic materials.

Quantitative restrictions: The foregoing observations provide a qualitative indication of some of the considerations that are required for the use of ceramics in engines. Applications of those results to engine design, however, require quantitative deductions to be made to convert laboratory results into predictive relations. For advanced ceramics, this cannot be done with the current technical literature. Quantitative comparisons of tribological data from different laboratories or merely different apparatus are frequently meaningless. Standardization is much needed in the specification and characterization of the ceramic material, in general, and of the tested specimen in particular. Further, the format for reporting data from experiments in tribology should be standardized to eliminate, as much as possible, device and operator dependencies that prevent comparisons of data. Without such consistency, it will be very difficult to establish the useful application ranges of ceramics, and impossible to establish predictive relations.

VI. LUBRICATION OF CERAMICS[87-118]

Effective control of the friction, wear, and fracture characteristics of ceramic-metal and ceramic-ceramic contact interfaces by means of lubrication is crucial to the success of many advanced technologies. Ceramics, being highly refractory, are relatively brittle and fracture easily, causing catastrophic failures. A knowledge of the lubrication process for this class of materials therefore is essential for their effective application.

A high quality commercial lubricant is a complex mixture consisting of a base oil and numerous chemical additives. The additives perform rather specific functions in the lubricant, such as inhibiting corrosion, reducing wear, delaying the oxidation of the oil, and reducing friction. The performance of each additive depends on its chemical reactions with surface material and with other molecules in the mixture. As a result, the formulation of a lubricant is quite specific to the material being lubricated.

The research issues in the lubrication of ceramics vary with the temperature range over which the materials are to be used. Therefore, research needs perhaps are best described according to the temperature categories of low temperatures (room temperature to 200°C), intermediate temperatures (200 to 600°C), and high temperatures (600 to 1500°C). Research issues within a given temperature range may further depend on the environment and the materials which are themselves dependent on the temperature. The issues also vary with different classes of lubricants: gases, liquids, solids, and coatings.

Temperature < 200°C: In the temperature range of ambient to 200°C, many components and systems today operate with liquid lubricants. Specialty solid lubricants such as graphite or molybdenum disulfide are also used. Application knowledge of these lubricants with metal systems is reasonably well understood. Many studies are being conducted on the mechanisms by which lubricant additives assist the lubrication of metals. However, very few studies have been done or are being conducted on the lubrication requirements of ceramics.

Ceramic tribo-elements usually are given a smooth surface texture, due in part to the need to remove microcracks from the surface. Hence, they are well suited for hydrodynamic (fluid film) lubrication. Under boundary lubrication conditions, ceramics, because of their relatively low thermal diffusivity, would tend to have much higher surface temperatures and resulting high interface temperatures.

Most liquid lubricants consist of base oils and additives. The lubricant formulation technology for metals is largely defined by the chemical reactivity of the additives with iron. The principal constituents of the major ceramic materials, however, are silicon, zirconium, aluminum, and boron in the forms of oxides, nitrides, and carbides. As a result, the iron-based additive technology may not be appropriate for ceramics, and it may be necessary to pursue an element-specific lubrication chemistry to obtain effective friction and wear control.

Temperature 200 - 600°C: The temperature range of 200 to 600°C has been and currently is very important for ceramic applications. Technologies embraced in this temperature range are high-temperature bearings, cutting tools, materials processing systems, and advanced combustion systems. Although lubricants in this temperature range have been studied intensely (Sliney and Johnson, 1968; Sliney, 1982; Sharma et al., 1983: Longson, 1983; Cosgrove 35 et al., 1959; Christy, 1982), a systematic data base has not been developed. In practice, a wide variety of lubricants have been used with a relatively small number of ceramic materials. Hot-pressed silicon nitride is the most-used ceramic material in various lubricant testing programs. Silicon carbide, zirconia, and reinforced alumina have also been evaluated. Titanium carbides and nitrides have been used for coatings, as have chromium oxides. Lubrication in the intermediate temperature range is complicated, not only because of the wide variety of applications and the different environmental factors involved, but also because of the variety of lubricant delivery systems, system compatibility, lubricant degradation, materials changes, lubricant-material reactivity, and diffusion. All these factors have a significant impact on system durability.

Temperature > 600°C: High temperatures need to be considered even when the average bulk temperature is not high. Asperity-asperity collisions may produce very high local temperatures at the asperity sites in ceramics. When the temperature goes above 600°C, very few conventional lubricants will function. The choice appears to be between high-temperature oxides, fluorides, mixed oxides, glasses, silver, gold, solid composites, and vapor-phase coating of chemically active species for short-period lubrication.

At high temperatures, coke and residue formation may be deleterious to some rubbing systems. Reactivity with the substrate needs to be balanced against corrosiveness. Because of the higher chemical reaction rates, active species may react and desorb rapidly, forming a corrosion product. Degradation of lubricant molecules and the formation of corrosive species is another serious problem. Given these constraints, vapor phase lubrication appears to offer a reasonable promise for an easy and economical way to lubricate ceramic materials at temperatures above 600°C.

At high temperatures, chemical reactivity between the lubricant and ceramic substrate is important. Calcium fluoride, barium fluoride, and lithium fluoride have high reactivity with many ceramic materials, such as alumina, zirconia, and silicon nitrides. New structures may form at the surface, resulting in either beneficial or deleterious effects on friction and wear. High temperature thermodynamic data, phase equilibria, and solubilities of mixed oxides and fluorides are currently not available. Thermodynamic models for predicting these relationships need to be developed.

The natural tendency for materials to adhere under sliding conditions increases with temperature. Successful lubrication of ceramic surfaces above 600°C must take into account the lubricant and substrate stability as a function of time. At high bulk temperatures and even much higher surface temperatures, the lubricant will undergo degradation and change. Diffusion within the substrate will increase with the temperature, causing surface segregation. Lattice vibrations will increase in amplitude, enhancing plastic deformation and dislocation mobility. When the temperature approaches half the melting point, deformation by creep becomes the dominant mechanism of the material under shear stresses. The lubricant has to maintain adhesive bonds with the changing substrate.

Lubricant resupply and the disposal of degraded lubricant at high temperatures is an additional concern in actual applications. In the absence of a liquid lubricant, disposal of wear debris from the surfaces could become a serious problem due to the resulting abrasive wear. Degraded lubricant could also form deposits on the surfaces, creating barriers to new lubricant supply.

Very few lubricants have been demonstrated to be effective and durable at temperatures above 600°C. Even fewer have been tested on ceramic surfaces, especially at those temperatures. There is, therefore, a need both to understand lubrication mechanisms and to find new lubricants for high-temperature applications.

Lubricant Types: Gases: Both inert gases and air have been used to provide fluid film support for bearings and other tribological contacts. Because of the limited load capacity and restrictions in terms of gas supply and bearing design, very few industrial systems use gas lubrication. Because no surface contact takes place under the air or gas bearing concept, the choice of the surface material is not as significant as in other cases. The key issue in this area has been the difficulty encountered during start-up and variable-speed operations, under which wear and adhesion become a problem.

Vapor-phase lubrication, via surface chemical reactions to form a strongly adhered protective film on the surfaces, is an attractive alternative (Pinto et al., 1984; Butler and Popovic, 1974; Buckley and Johnson, 1959). The concept is to deliver vapor-phase-reactive compounds at high temperatures to the rubbing contacts. The subsequent reaction film, if tenacious, will protect the surfaces for a short time against high shear stresses. Phosphate esters and melissic acid have been found to be useful for steel surfaces at temperatures up to 700°C. Liquid phosphate esters have also been used with a ceramic engine prototype and were found partially satisfactory. Klaus (1986) has demonstrated that phosphate esters deposited between 300 and 900°C on steel surfaces are capable of forming a tenacious film with thickness on the order of 1000 molecular layers. The deposition rate and reaction rates are dependent on oxygen partial pressure, temperatures, and substrate materials. It has been demonstrated that a low concentration of 0.2 percent by weight of tributyl phosphate (TBP), tricresyl phosphate (TCP), and diphenyl-di-tert-butylphenyl phosphate (DBTBPP) in the vapor stream is sufficient to protect the steel surfaces at 370°C.

The attractiveness of the vapor-phase lubrication concept lies in the simplicity and ease of lubricant delivery. A minute amount of lubricant can be metered out over a period of time to protect the wearing surfaces. In the heat engine case, the lubricant may be added in the fuel and deposited directly on the cylinder liner during combustion.

Research issues in this area involve the need for development of a basic understanding of the chemical reaction mechanisms, the need to determine the nature of the reaction products, and the need to establish the reactivity of the potential lubricating materials with the various ceramic substrates.

Lubricant Types: Liquids: The use of liquid lubricants in heat engines in the temperature range of 200 to 600°C is limited. At the same time, liquid lubricants are desirable since they can be used to flush the system, are available in a useful form to lubricate the engine during the start-up at low temperatures, and may be used to remove wear debris. For heat engines, even though the temperatures at the piston ring and cylinder liner will approach 400 to 600°C, the engine sump temperature may only be 150 to 200°C. Very few liquid lubricants can operate above 300°C for any substantial length of time. However, there are two possible concepts which might be useful for providing lubrication at these temperatures; controlled burning of lubricants and a combination of liquid and solid lubrication. In the latter case, the liquid lubricant would be used under a certain temperature range. When the temperature rises above a preset value, the liquid lubricant flow would be shut off and the solid lubricants would begin to function. A very stable liquid lubricant therefore is needed.

There is an extensive literature as well as a significant amount of industrial experience on metal lubrication via additives in liquid base oils. For ceramics, however, very few similar studies have been conducted. Shimauchi et al. (1984) conducted both laboratory and prototype single-cylinder engine endurance tests to assess the effects of liquid lubricants on ceramic components. They concluded that different liquid lubricants affected the tribological performance of various ceramic surfaces significantly. The tests were conducted using different liquid lubricants on various material pairs under controlled laboratory tribological conditions. The materials consisted of various plasma-sprayed coatings 0.2 mm thick (including chromium oxides, carbides, titanium and tungsten carbides, zirconia, and chromium oxide with vanadium carbides). Only one oil, an ester fluid without additives, functioned reasonable well.

Data from Garrett's turbo-compound engine program also show that the choice of liquid lubricant is of paramount importance (Keiser and Castor, 1981). That program tested an extensive list of materials and lubricants at 650°C. Again, esters appeared to be a promising candidate to control friction and wear of various superalloys, ceramics, and composites. An extensive data base like this yields valuable information through trial and error, but little fundamental understanding is gained. Why a particular ester family functioned well and other esters would not function under the same conditions was not clear. Fundamental studies will yield a knowledge base from which future lubricants and additives for ceramics may be developed.

The key issue in the area of liquid lubricants for heat engines is the basic understanding of surface chemical reactions between the liquid lubricants and the ceramic surfaces. For silicon carbides and nitrides, a limited data base of silicon chemistry exists in the geochemistry and semiconductor areas. For example, water reacts rapidly with silicon through hydrolysis reactions and forms various hydrides with different friction and wear characteristics. In fact, the reactivity of water with many ceramic materials has long been recognized and utilized in ceramic machining. Zirconia, on the other hand, may not respond to water or other silicon-specific chemistry. In metal systems, controlled chemical reaction rates have proved to be a key for effective lubrication. No corresponding data base exists for ceramics.

The availability of additives and the understanding of additive mechanisms at high temperatures is critical (Fehrenbacher, 1985). Oil evaporation, degradation, degradation products, degradation product corrosiveness with materials, and the effective control of emissions are other significant technical challenges in this area. A detailed discussion of some aspects of this subject has been presented by Fehrenbacher (1985).

At high temperatures above 600°C, there are also lubricants existing in the liquid state. However, most of these lubricants are solids at room temperature. Thus, before a device lubricated by high temperature lubricants such as silicates and borates can be utilized, the sliding interface must first be heated. This limits their potential applications.

Lubricant Types: Solids: One interesting aspect of ceramic lubrication is that, to date, very few studies have been conducted using solid lubricants on ceramic surfaces. The majority of the studies of ceramic materials in the form of either coatings or solid materials are tested at room temperature or moderate temperatures (300°C) with a liquid lubricant. Several studies of ceramic materials have been reported (Shimauchi et al., 1984; Keiser and Castor, 1981).

There are many studies related to the use of solid lubricants for metals under severe environments (American Society of Lubrication Engineers, 1971, 1978, and 1984; Weilbach, 1982). A number of reports (Gardos, 1982; Yonushonis, 1980 and 1983; Ling, 1985; Lucek, 1979; Dayton and Sheets, 1976; Fusaro, 1982 and 1983) specifically examine solid lubricants for ceramics. Solid lubricants used in these studies are varied but mainly consist of layer lattice solids (graphite, molybdenum disulfides, graphite fluorides, tungsten sulfides, etc.) polyimides, oxides, and polytetrafluorethylene (PTFE).

While there are many solid lubricants, the choice of solid lubricant delivery method is critical to successful application. Solid lubricants can be supplied through transfer films, coatings, liquid suspension, gas suspension, bonded films, powder compact, surface modification, or burnished coatings. In many of these methods, lubricant-substrate bonding, adhesion, and reactivity are crucial to the success of lubricant delivery. Again, experience with these methods and materials combinations is mostly with metal systems. Very few ceramic substrates have been studied. Based on metal system experience, the critical issues are seen to be lubricant-substrate or lubricant-surface adhesion; lubricant-surface reactivity and bonding strength; rate of adhesion and reaction; and lubricant film stability, strength, and durability.

The effectiveness of the lubrication obviously depends on how readily and how strongly the solid lubricant adheres to the surface or substrate. In the case of solid lubricants carried by gas, the lubricant has a relatively short period of time to adhere to the surface. Once at the surface, the bonding strength of the solid film with the substrate is important. Often this is achieved through the chemical reaction between the solid lubricant and the surface or substrate materials. In ceramics, the adhesion and reaction may be a problem with many solid lubricants. The high-temperature kinetics of solid lubricants with ceramic surfaces have simply not been tested. In many cases, depending on the method of delivery, the relative rates of adhesion and reaction with the amount of time allowed by the rubbing action may be important. At high temperatures, desorption or other unfavorable reactions such as phase change or new compound formation may also interfere with the normal processes of lubrication.

Because of the wide variety of materials and potential solid lubricants, and also the additional variation introduced by the methods of lubricant delivery, a systematic assessment of lubricant-ceramic combinations is needed. Table III lists some commercially available solid lubricants and their temperature limitations with metal systems. Notice that most solid lubricants in air have a maximum operating temperature in the range of 200 to 500°C. These are, however, adequate for some heat engine applications. Table IV lists the estimated life of some of the solid lubricants in the piston ring zone at projected heat engine conditions and temperatures.

The basic mechanisms of solid lubrication, even at low to moderate temperatures, are not well understood. Graphite and MoS_2 have been studied extensively. Other higher temperature materials have not been systematically investigated. At high temperatures (600°C), reactivity of the lubricant with the substrate and the degradation of the lubricant either through oxidation and/or thermal degradation complicate the mechanistic understanding. Under tribochemical conditions, where enhanced reaction rates arise because of bond rupturing and the presence of the dangling bonds, many reactions occur that normally would not take place. These areas of surface adhesion and chemical reactivity are largely untouched in metal systems.

Testing of ceramic materials at high temperatures (650°C) has been very limited (Longson, 1983; Weilbach, 1982; Gardos, 1982; Yonushonis, 1980 and 1983). Lubricants used include cesium molybdate complex, gallium-indium-tungsten diselenide (Ga/In/WSe_2) compact, tungsten disulfide, polyimide, metal-free phthalocyanine, graphite, and calcium fluoride-barium fluoride eutectic in nickel foam. Ceramic materials used were primarily silicon nitrides and silicon carbides. Most of the test results reported poor performance compared to conventional metal systems under approximately the same speed and load conditions. The ceramic counterpart at high temperatures typically lasted 1 or 2 hours, compared with thousands of hours of operating time for metals.

One of the technical challenges mentioned by many researchers involved in ceramic bearing testing with solid lubricants is the rapid rise in temperatures at the interface. Ceramics have lower thermal diffusivity than metals. Ceramics, being brittle, fracture relatively easily, producing high friction under boundary lubrication conditions. Frictional heating can produce extremely high flash temperatures and interfacial temperatures. For higher temperature lubricants, such as oxides (bonded $PbO-SiO_2$) or inorganic salts, the friction often is quite high (coefficient of friction being about 0.2 to 0.8). Many high-temperature solid lubricants such as glasses and fluorides are brittle and abrasive below their softening-point temperatures. Thus, a combination low-temperature lubricant and high-temperature lubricant will be necessary.

<u>Prospects for Lubricated Ceramics</u>: There is an urgent need to develop an effective lubrication system so that ceramics can be utilized effectively. To accomplish this goal, research is required in several critical areas:

(1) Lubrication Mechanisms

- Low temperature (bulk temperature) applications will create the largest short term markets for structural ceramics. The chemical reactivity between hydrocarbon lubricant structures and ceramic surfaces needs to be defined. The mechanism of reaction and rate of reaction under boundary lubrication conditions should be studied to examine the structural effects, functional group influence, and physical properties effects.

- Surface forces at ceramic surfaces need to be measured. The additional double layer forces at ceramic surfaces will affect adsorption, lubricant-substrate adhesion, wetting, and reactivity.
- Lubrication behavior of solid lubricants at high temperatures needs elucidation. Effects of diffusion, segregation, reactions, and degradation on adhesion and surface protection need careful study. The formation of new phases and reaction products at high temperatures need to be defined both with and without tribocontacts.
- Thermodynamic equilibrium of phases and solubilities of lubricant and substrate need to be determined experimentally, and models need to be developed to predict these equilibria.
- Degradation mechanisms of lubricants and their influence on friction and wear over the temperature ranges of interest should be studied.

(2) Lubricant Development

- Element-specific chemistry-based additives which provide friction and wear control through the formation of protective films need to be developed.

- High temperature antioxidants that can survive exposure to 400°C for a short period of time should be developed. Different mechanisms may be operative in this temperature regime.
- For heat engine applications, high temperature (400°C) ashless dispersants and acid neutralizers are needed.
- Novel chemical processes for synthesizing high temperature liquid lubricants need to be explored.

(3) Lubricant Delivery and Disposal Research

- Vapor phase deposited lubrication for short duration protection is a very attractive concept. Functionality, reactivity, deposit control, and reaction mechanisms need to be investigated systematically.
- Impregnation of material substrates by lubricants in the form of coatings, physical vapor deposition, ion beam mixing, and self-lubricating composites should be explored.
- Spent lubricant and wear debris will be deleterious to system durability. Mechanical design changes to prevent debris accumulation, as well as chemical means to remove debris, may be critical to the lubricant selection.

In general, the fundamental information needed for application to ceramics lubrication research is lacking. While the technology for metal lubrication has matured, the detailed mechanisms are not fully understood. Thus, information transfer from existing technologies to ceramic lubrication may be slight. A systematic effort needs to be established to define the surface energy, surface reactivity, surface composition of simple single crystals with different molecules under different environmental factors.

VII. RECOMMENDATIONS

GRI has a rare opportunity to advance the utilization of natural gas via advances in gas-fired prime movers. Prompt action on the part of GRI may establish natural gas as the fuel of choice for high efficiency, high temperature heat engines and for high durability cogeneration applications. To exploit this opportunity, GRI must accelerate research in several principal areas of tribology: (1) A ceramic materials selection guide must be developed for use in designing for optimum wear life under gas-burning conditions; (2) Lubrication research must be pursued to develop a combination of lubricant chemistry, engine materials, and additives that will function under high temperature gas-burning conditions; and, (3) Effects of engine material microstructure on wear resistance, surface reactivity, and lubrication requirements in gas combustion environments must be determined.

The key goals to be attained in the successful use of advanced gas-fired engines in cogeneration and transport applications are increased efficiency and durability. Currently, attainment of both of these goals is limited, not by theoretical designs, but by the availability of materials and lubricants capable of sustaining the relatively extreme conditions demanded by the advanced high temperature designs. Current engines are already designed to utilize the best metal alloy materials near the operating limits of their material properties. Thus, the need for still higher operating temperatures demands the use of advanced ceramics in engines.

Ceramic materials are generally well characterized in terms of mechanical properties. However, most of these properties are measured under static, nontribological conditions. Application of ceramics as wear components requires friction and wear data that are not well documented in the current literature. Results specific to gas-burning environments are extremely scarce.

Studies are badly needed in the four general areas as listed in Table V. The development of data on the sliding wear and friction characteristics of ceramics is an especially high priority need. These data have both immediate and basic applications. Such data, for example, will be valuable in surmounting such problems as the wear of the apex seal/housing couple in rotary engines. Further, these data will serve the more basic, longer term function of developing an understanding of wear mechanisms for ceramic materials. This understanding will be necessary for the development of predictive models of wear and durability which may be used in the design of engine components. To accomplish these goals, the wear characteristics of advanced ceramic materials must be mapped as a function of several operating conditions, including speed, load, temperature, and environmental conditions, under both dry and lubricated wear and in the presence of gaseous combustion products. Furthermore, a detailed understanding of microstructural effects needs to be developed.

A comparably high priority should be given to the development of lubricants for preventing or reducing the wear of ceramic materials. Lubrication is a much overlooked problem in discussions of the applications of ceramics in tribological systems. This circumstance results partly because of a lack of appreciation of the functions of a lubricant and partly because <u>how</u> a lubricant works is not fully understood by the component designers who are not necessarily tribologists or schooled in tribology. Lubricants are used primarily to reduce friction and wear by forming a protective film between the tribosurfaces. In the simplest concept, this film could be formed by any flowing material and would work merely by separating the solid surfaces. However, in most cases where lubrication is needed in an engine, this simplistic form of lubrication is not applicable. Instead, the lubricating film must be formed as a chemical reaction product between the applied lubricant and the substrate material. It is this role of chemistry that is most frequently neglected in the considerations given to the use of ceramic materials in tribo-systems. Lubricants are also used to clean the surfaces of the tribo-materials by removing the wear debris that would otherwise contribute to additional wear. How this function will be performed at elevated temperatures has not yet been established. Research is needed on the general mechanisms of lubrication for ceramics, the formation of deposits, the stability of the formulated lubricant at high temperatures, and the influence that gas combustion products may have on lubricant degradation. Such factors are important for durability, efficiency, and scheduled maintenance intervals.

Wear processes inherently involve the surface properties of materials. Hence, those properties relating to strength, yielding, cracking, or flowing of the material are especially significant contributors to the severity of wear produced in the tribocontact and to the nature of the wear mechanism. As a result, data on surface hardness, fracture toughness, creep strength, and surface ductility are needed to characterize or to determine the role of these properties in wear processes. How these characteristics depend on temperature and how they affect the accumulation of wear damage must be considered especially in designs requiring high durability of long component wearlife. Further, such data are much needed to understand the wear mechanisms of ceramics under conditions prevalent in engine operations.

The environmental factors associated with the combustion processes in the engine also create tribochemical conditions that cannot be neglected. At the temperatures generated by the combustion of the fuel, most materials, including ceramics, will exhibit some degree of chemical reactivity. Specifically, oxygen and the fuel's combustion products can be expected to react with the substrate. Data on the stability of ceramics against such reactions are scarce. Likewise, data on the influence that those reactions may have on wear mechanisms and wear rates are very limited. To fill these gaps in the understanding of environmental effects, detailed and systematic studies of oxidation resistance and the reactivity of ceramics with gas combustion products should be pursued. Further, such studies should be done concurrently with wear tests to determine their roles in wear mechanisms and rates.

Gas-fired engines have a viable future as producers of useful mechanical and electrical power. The technological barriers impeding the realization of that future are not so extreme that they cannot be surmounted with a reasonable effort in the near future. It is apparent that, among all the alternatives, ceramic materials have the greatest potential for increasing the durability and efficiency of gas-fired engines to the levels necessary to achieve the successful utilization of natural gas prime movers. Advances in the tribology of ceramic materials represent the critical, pivotal, developments needed for that success.

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Table I: A summary of the general material properties needed for advanced gas-fired prime movers.

<u>Thermal Characteristics</u>
- High melting point
- Low thermal conductivity and diffusivity
- Low thermal expansion
- High thermal shock resistance

<u>Mechanical Properties</u>
- High flexural strength
- High fracture toughness
- Low density

<u>Tribological Performance</u>
- Low friction
- Low wear
- Long wearlife

Table II: A summary of the major wear mechanisms of alumina, silicon nitride, silicon carbide, and partially stabilized zirconia, as cited in the technical literature.

Condition	Al_2O_3	Si_3N_4	SiC	PSZ
Ambient	Fracture Delamination Plast.deform. Grn.bnd.crack Fatigue	Delamination Plast.deform. Grn.bnd.crack Fatigue	Fracture Plast.deform. Grn.bnd.crack	Delamination Therm.stress Fracture Fatigue
Lubr. or wet	Plast.deform. Fracture Tribochemical	Plast.deform. Fracture Tribochemical	Plast.deform. Fracture	Therm.shock Tribochemical
Vacuum or Hi.Load	Adhesion	Fracture	----	----
Hi.Temp. 400°C to 1000°C	Plast.deform. Therm.stress	Fracture Therm.shock Tribochemical	Fracture Therm.stress	Therm.stress

Table III: Commercial Solid Lubricants

Lubricant	Acceptable usage temperature with metals, °C			
	In Air		In N_2 or Vacuum	
	Minimum	Maximum	Minimum	Maximum
molybdenum disulfide	-240	370	-240	820
polytetrafluorethylene	- 70	290	- 70	290
fluoroethylene-propylene	- 70	200	- 70	200
graphite	-240	540	unstable in vacuum	
niobium diselenide			370	1320
tungsten disulfide	-240	430	-240	820
tungsten diselenide			370	1320
lead sulfide		480		
lead oxide		650		
calcium fluoride - barium fluoride eutectic	430	820	430	820

Table IV: Estimated Life of Solid-Lubricated Piston Rings

Material	Best K[a]	T_{max} (°F)	Estimated Life[b] (hours)
Unlubricated ceramic	12×10^{-8}	1800	12
Plug-lubricated ceramic	1.2×10^{-8}	1000	120
Bonded film	3×10^{-8}	700	0.4
Carbon graphite	2×10^{-8}	1000	100
Filled Teflon	6×10^{-8}	500	17
Polyimide	18×10^{-8}	800	14
NASA hi-temp film	30×10^{-8}	1600	2.3
Metal matrix composite	100×10^{-8}	1000	1.7

[a] Dimensionless wear coefficient, $K = \frac{HV}{DL}$, H = hardness, D = distance traveled, L = Load

[b] Life based on 0.020 in. wear under typical conditions, P = 300 psi

Source: Owens, Southwest Research Institute, San Antonio, Texas in Ling, F. F., "Fundamentals of high temperature friction and wear with emphasis on solid lubrication for heat engines," U. S. Army ARO Contract DAAG 39-84-M-0479, June, 1985.

Table V: Recommended topical research areas to advance the development of gas-fired prime movers.

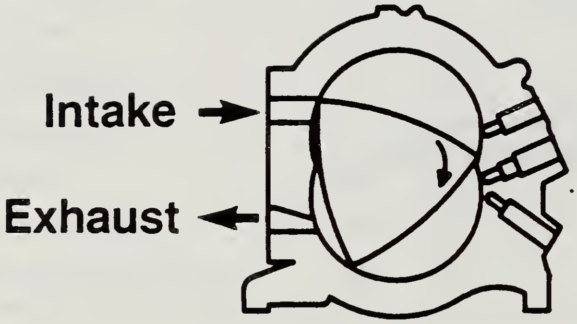
Performance
- Dry and lubricated wear and friction properties
- Wear regimes and rates
- Wearlife
- Mechanisms of friction and wear
- Materials compatibility

Wear Protection
- Lubrication of ceramics
- Additives for advanced lubricants
- Deposit control
- Influence of gas combustion products

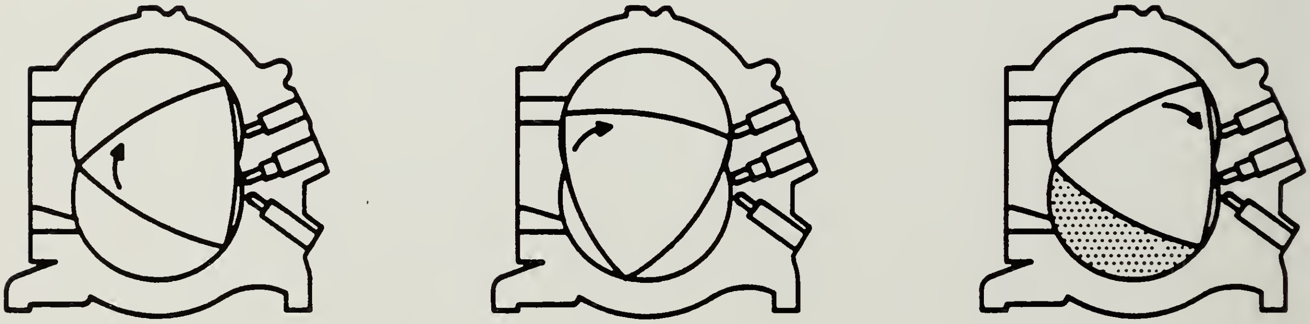
Surface Reactivity of Ceramics
- Oxidation resistance of ceramics
- Interaction with gas combustion products
- Environmental effects on surface microstructure

Surface Strength
- Surface hardness
- Fracture toughness
- Creep strength
- Surface ductility

Fig. 1: Working cycle of a rotary engine



(a) Intake (b) Compression



(c) Combustion (d) Power (e) Exhaust

Fig. 2: Primary wear components in a reciprocating engine

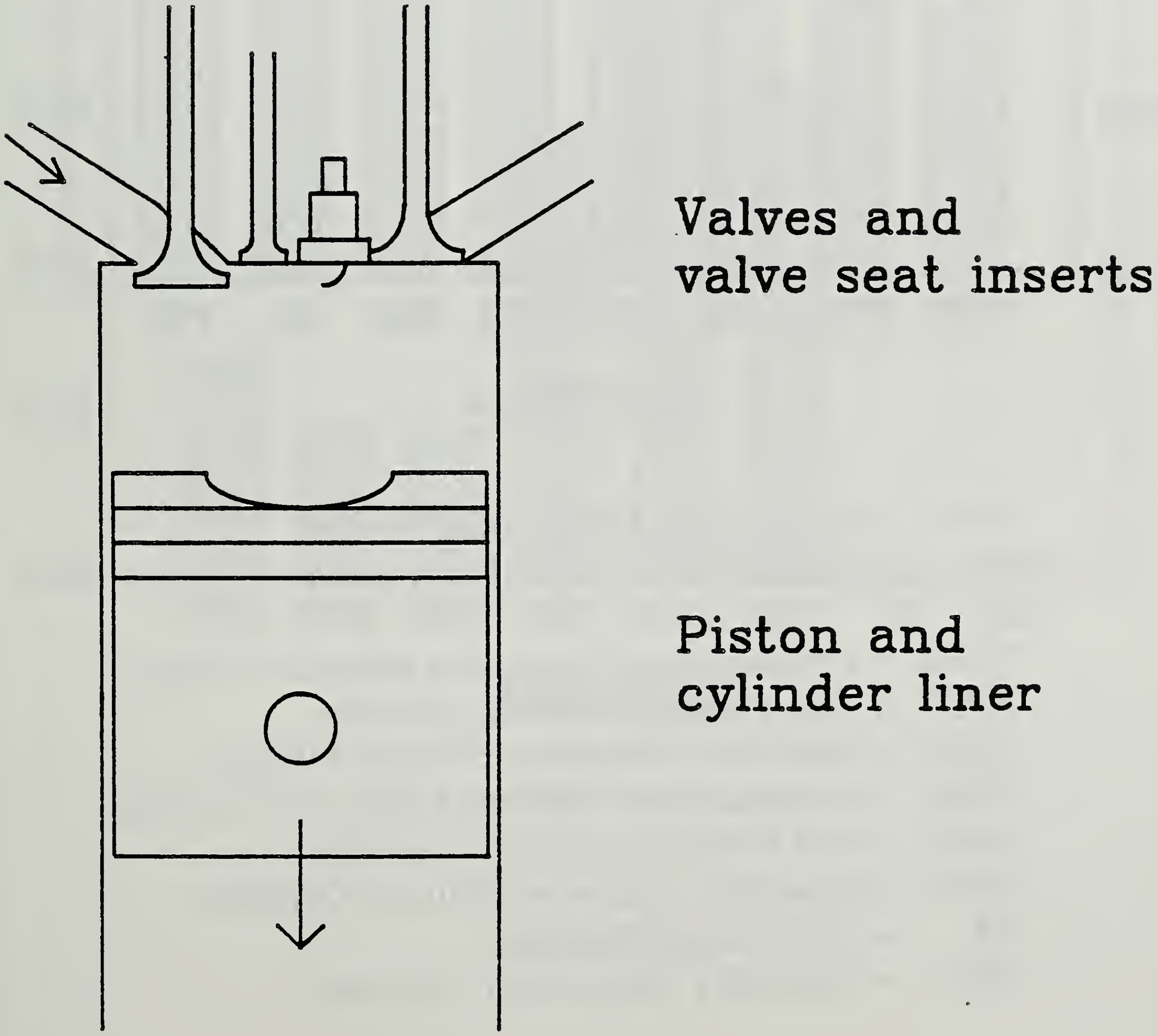
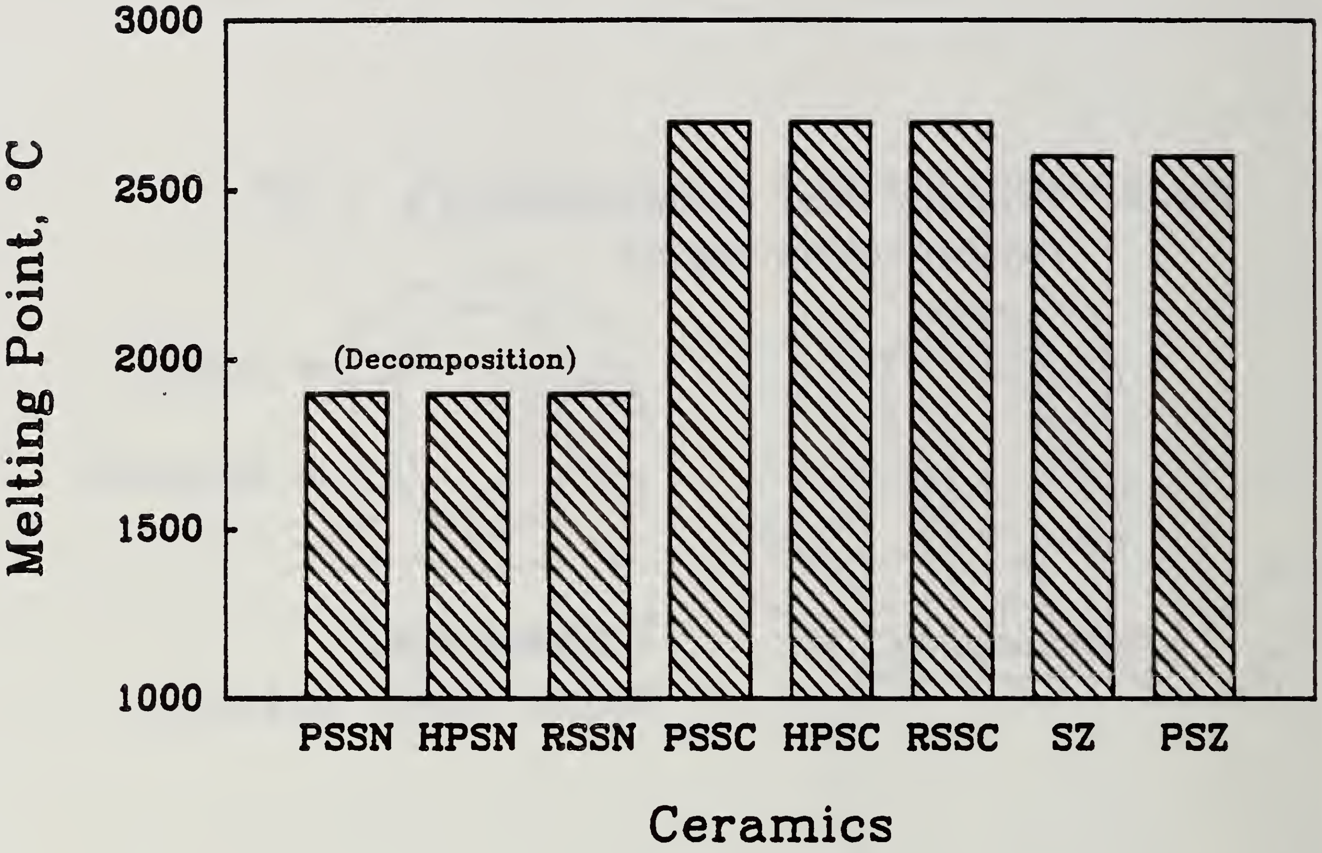


Fig. 3: Melting points of selected ceramics



Note: The silicon nitride materials decompose rather than melt

PSSN = Pressureless Sintered Silicon Nitride
HPSN = Hot Pressed Silicon Nitride
RSSN = Reaction Sintered Silicon Nitride
PSSC = Pressureless Sintered Silicon Carbide
HPSC = Hot Pressed Silicon Carbide
RSSC = Reaction Sintered Silicon Carbide
SZ = Stabilized Zirconia
PSZ = Partially Stabilized Zirconia

Fig. 4: Thermal conductivity of selected ceramics

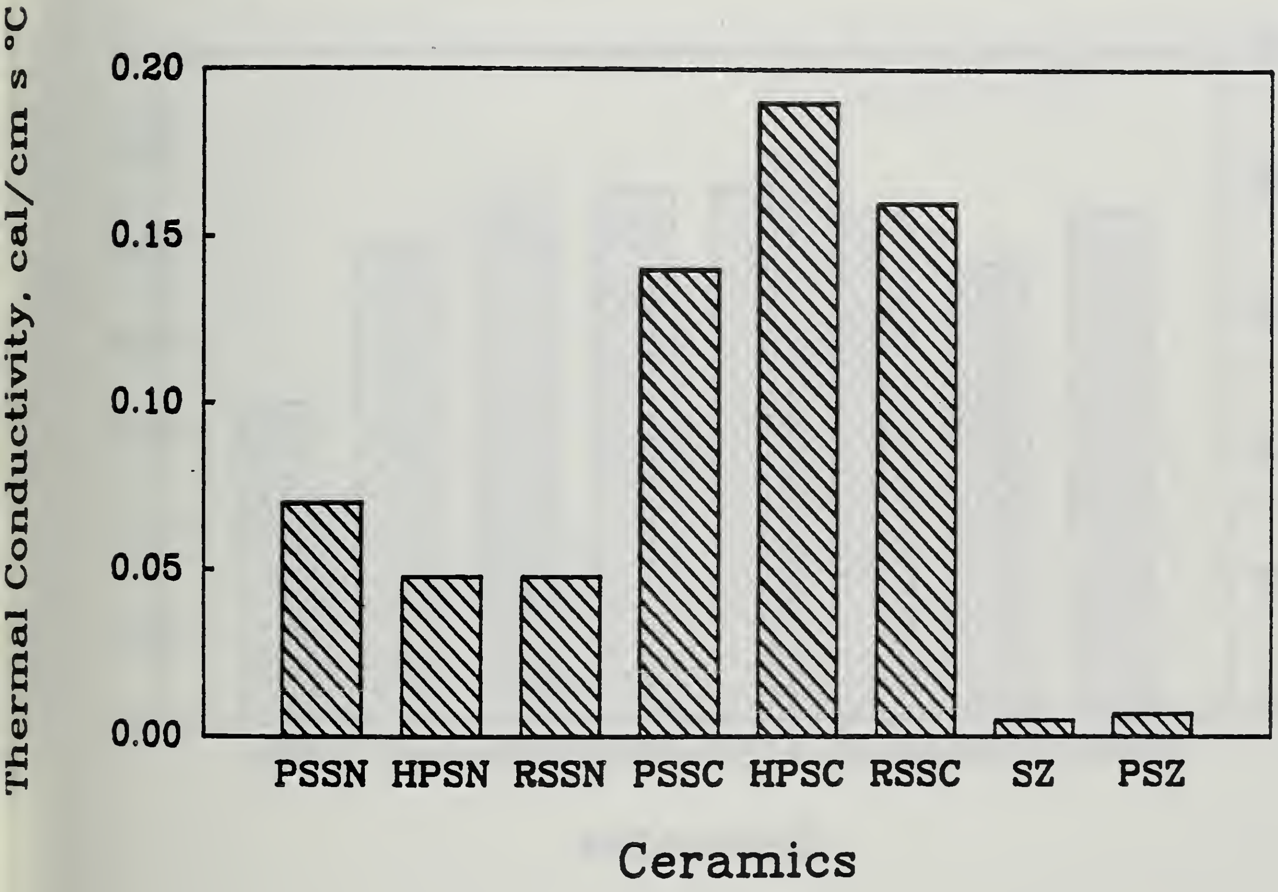


Fig. 5: Heat capacity of selected ceramics

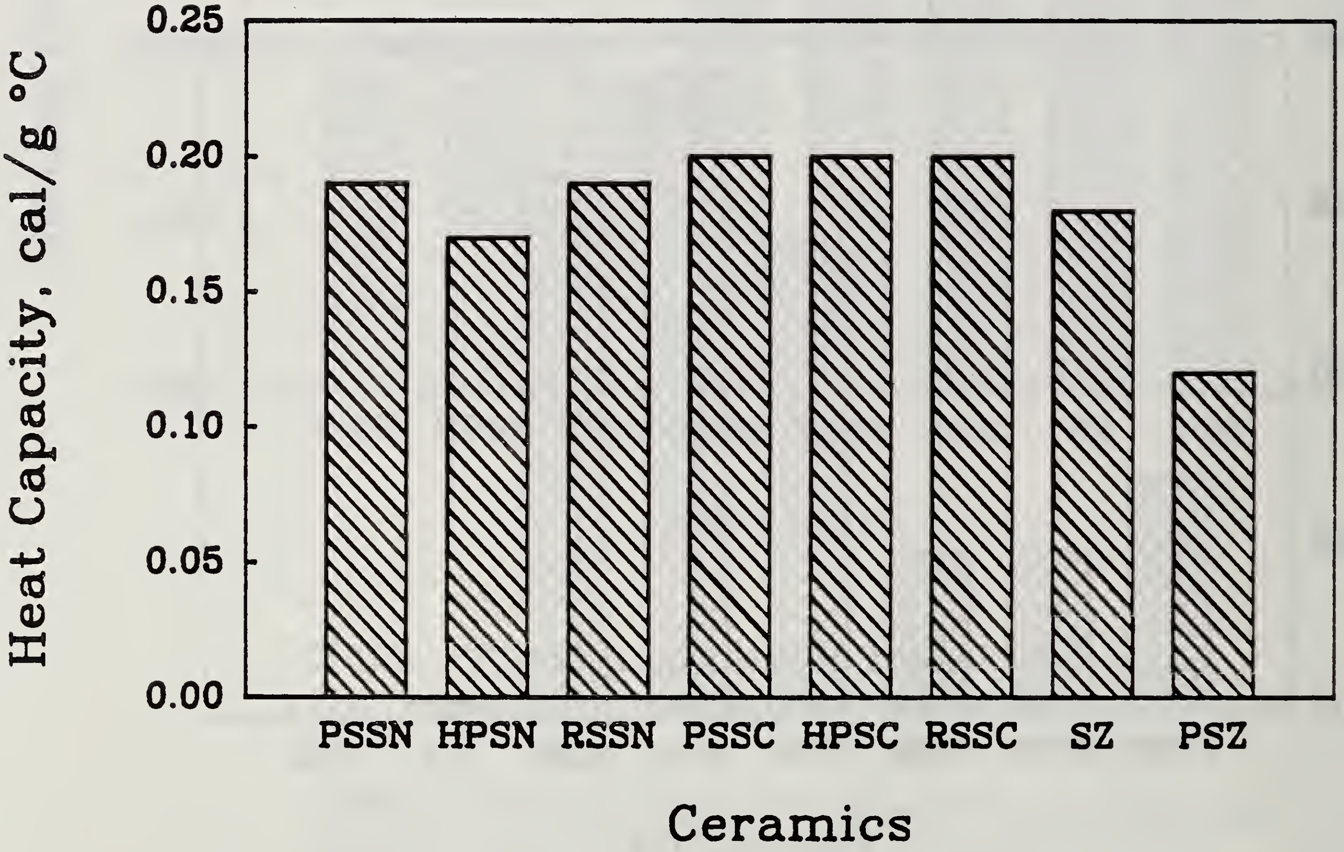


Fig. 6: Thermal diffusivity of selected ceramics

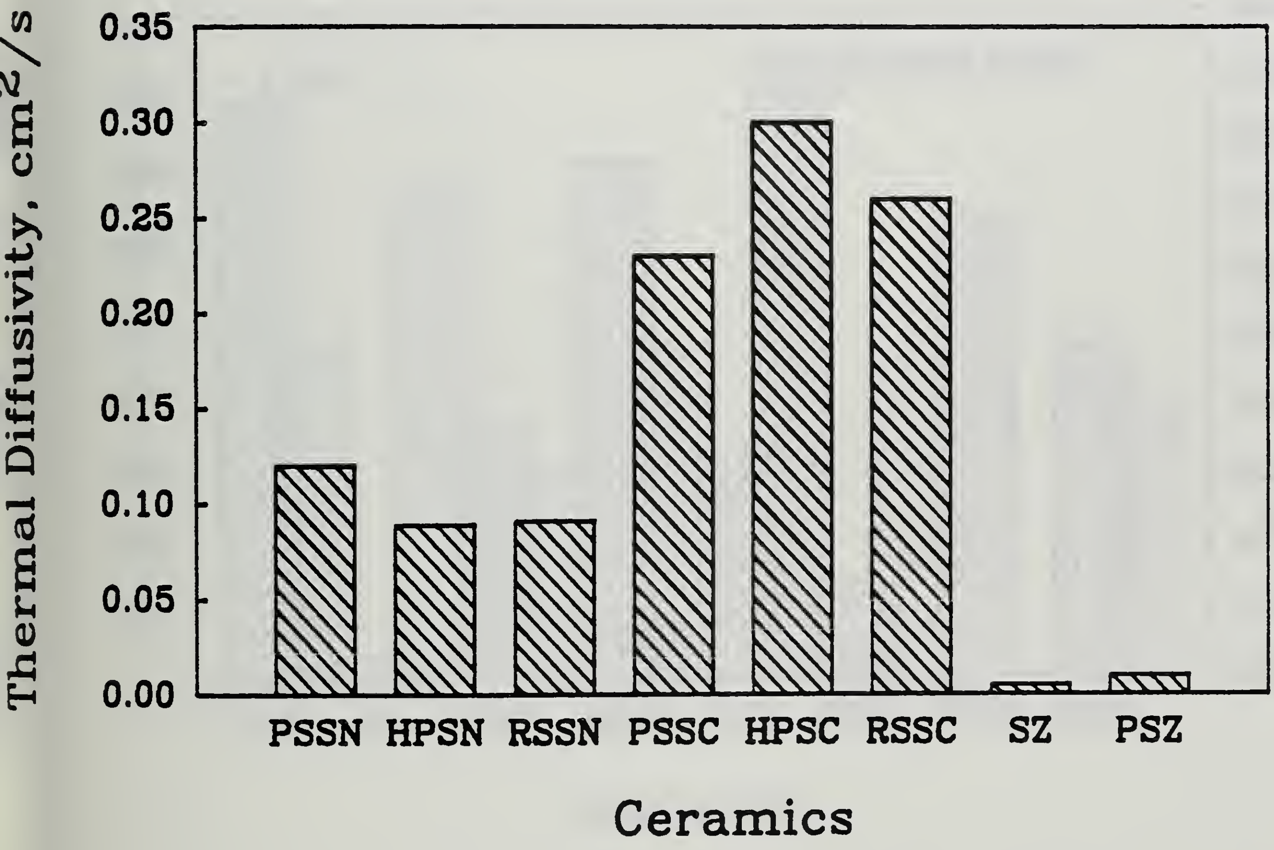


Fig. 7: Flexural strength of selected ceramics at room temperature

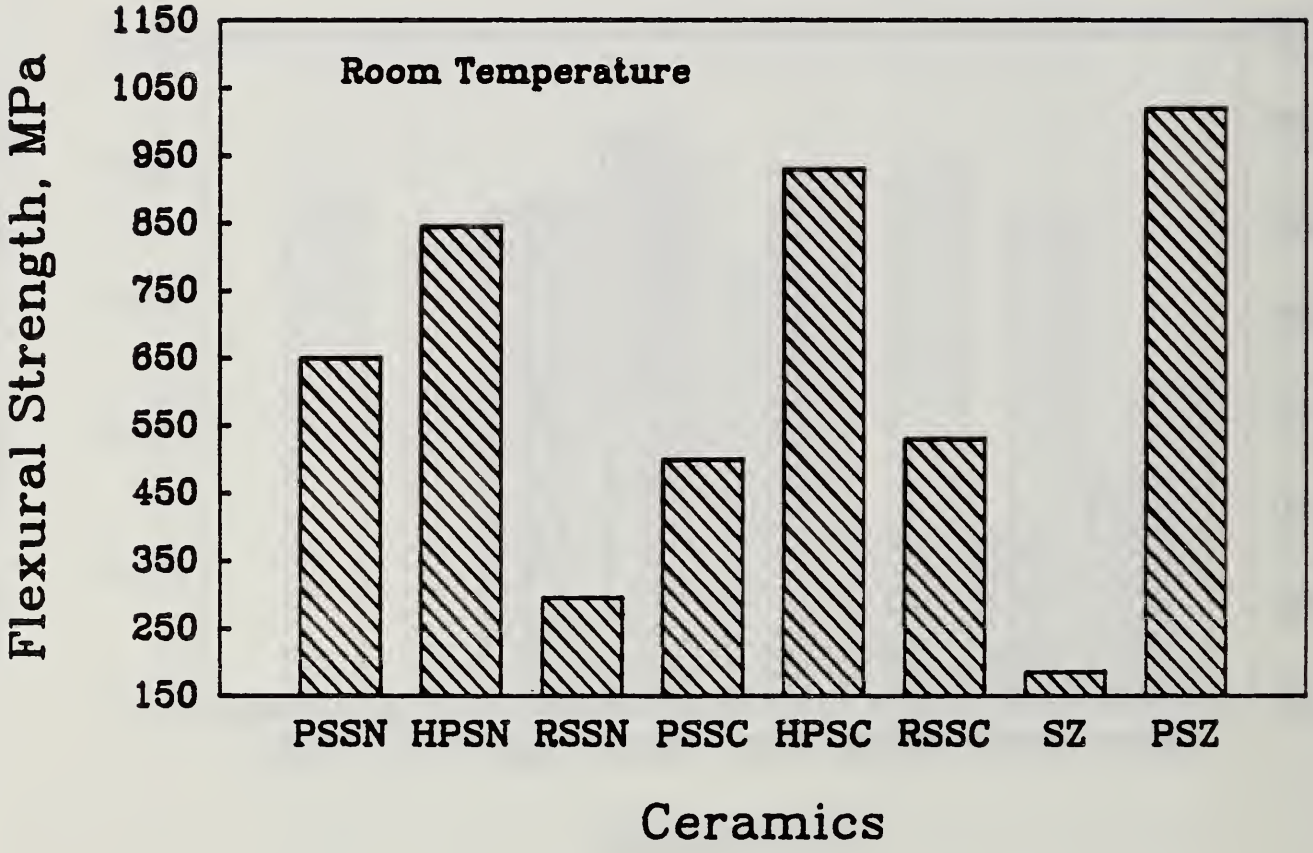


Fig. 8: Flexural strength of selected ceramics at high temperature

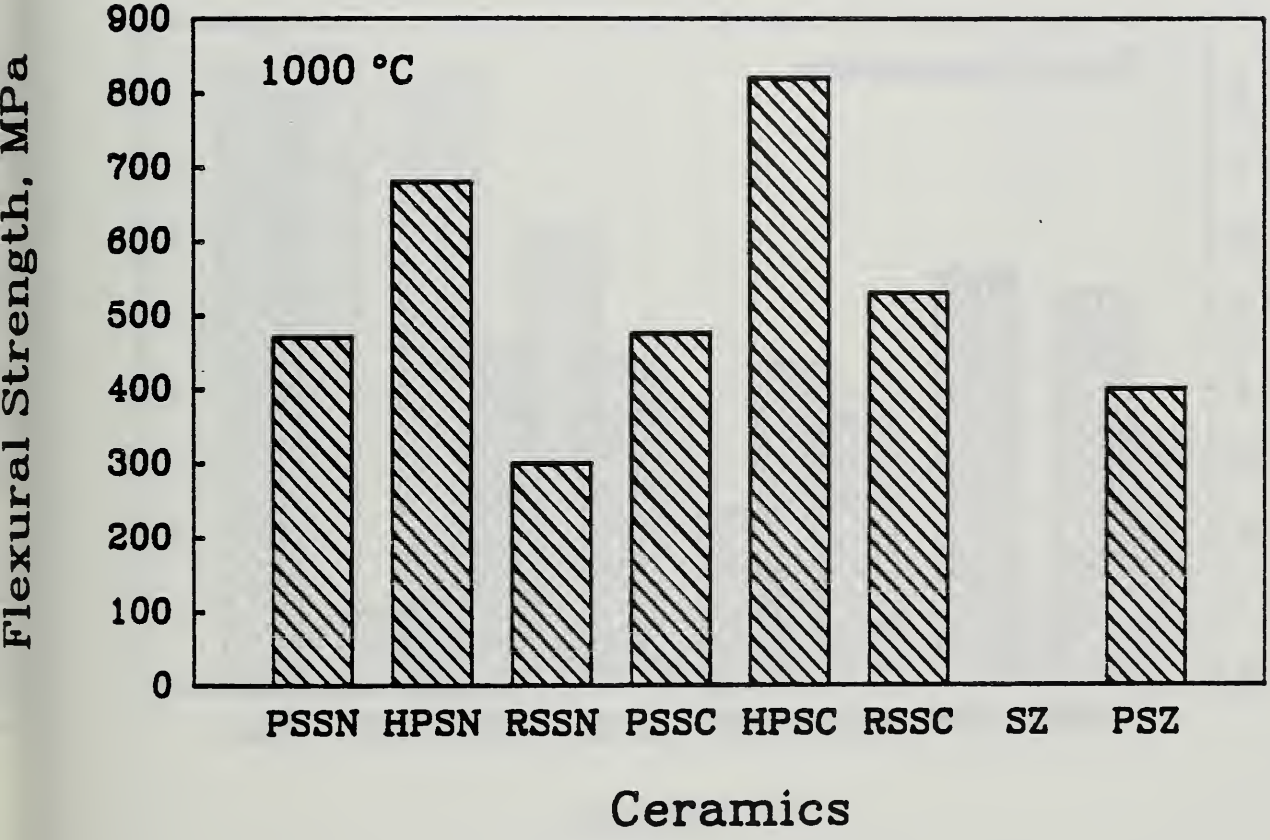


Fig. 9: Fracture toughness of selected ceramics

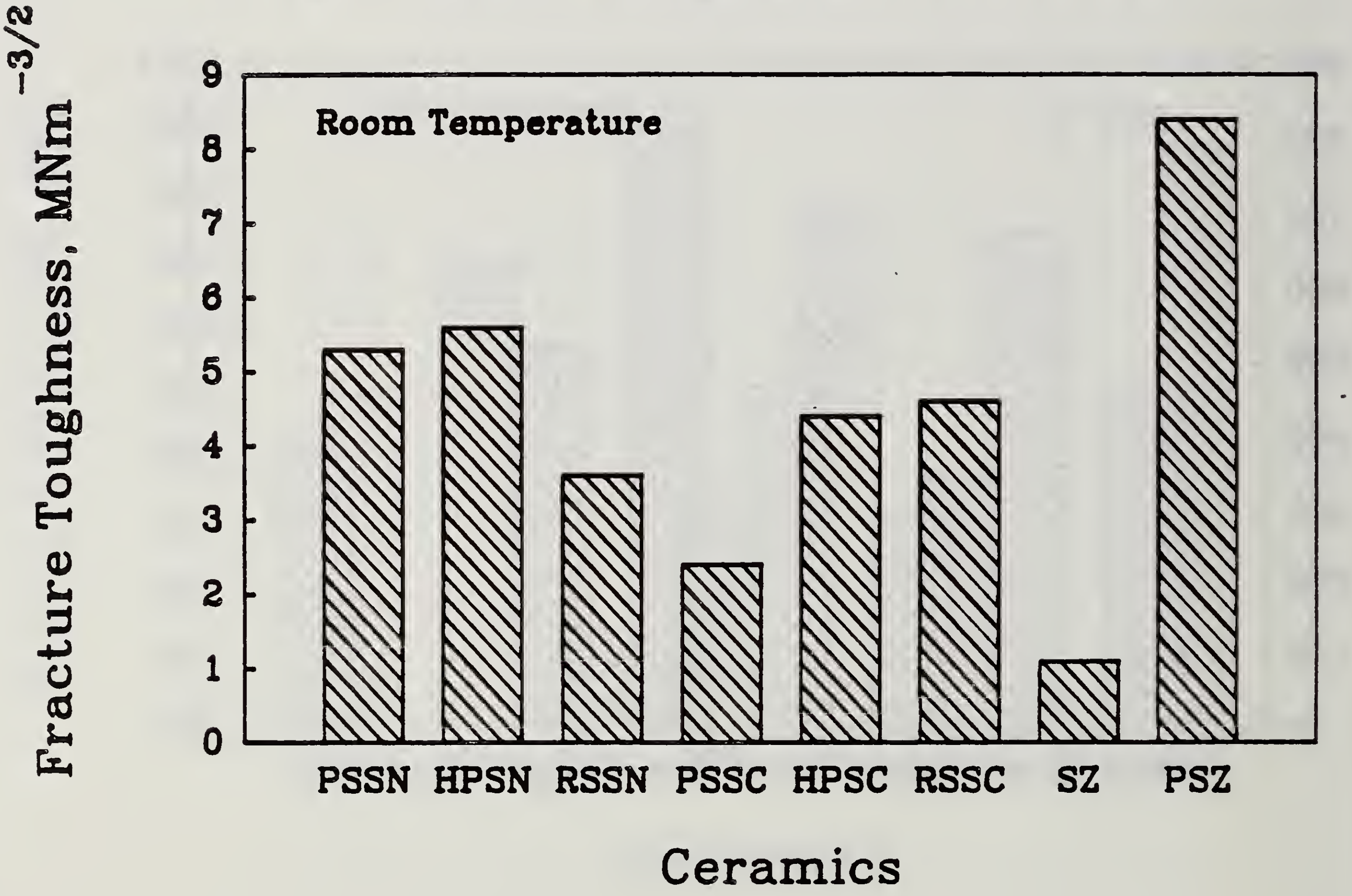


Fig. 10: Thermal shock resistance of selected ceramics

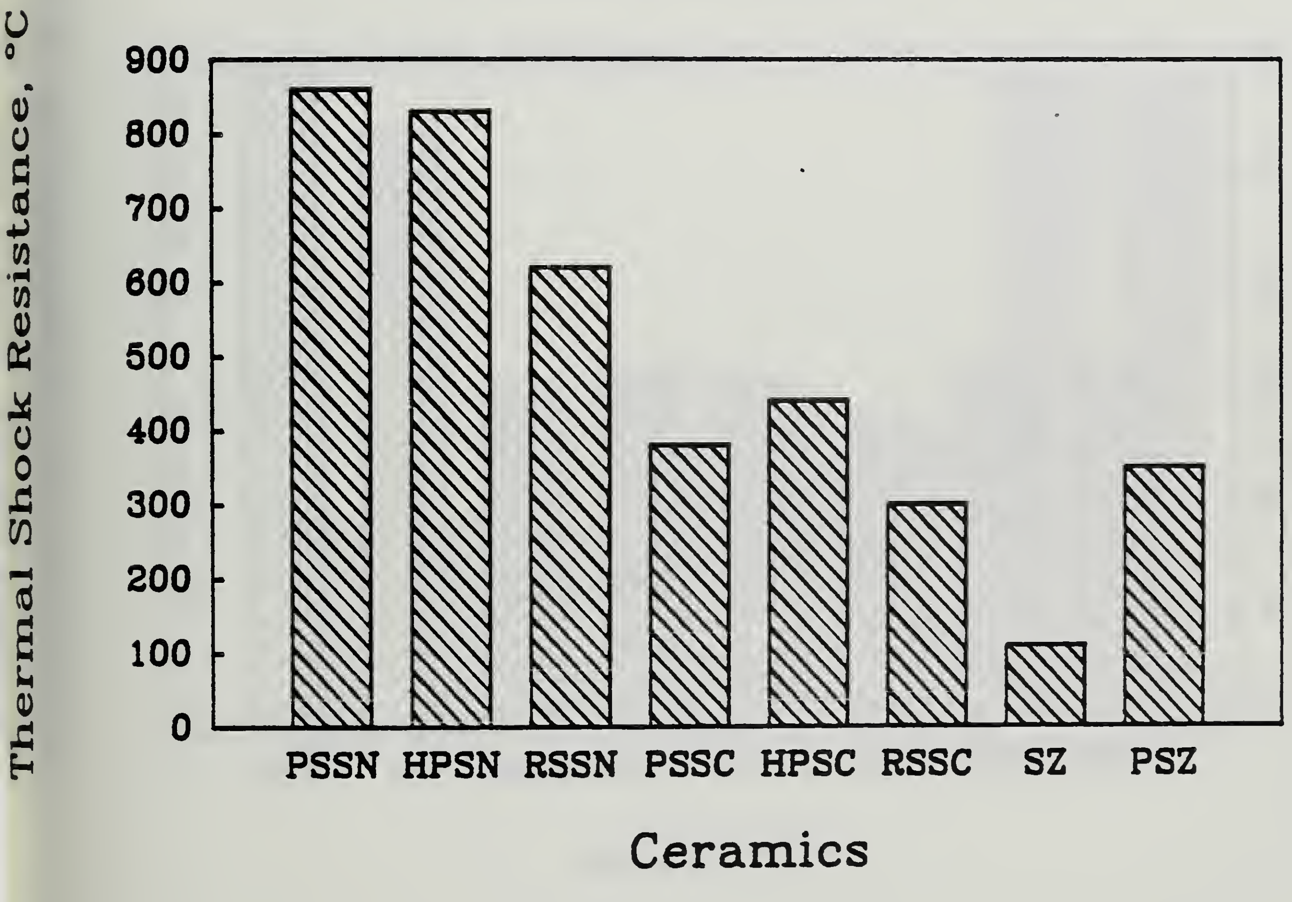


Fig. 11: Mass density of selected ceramics

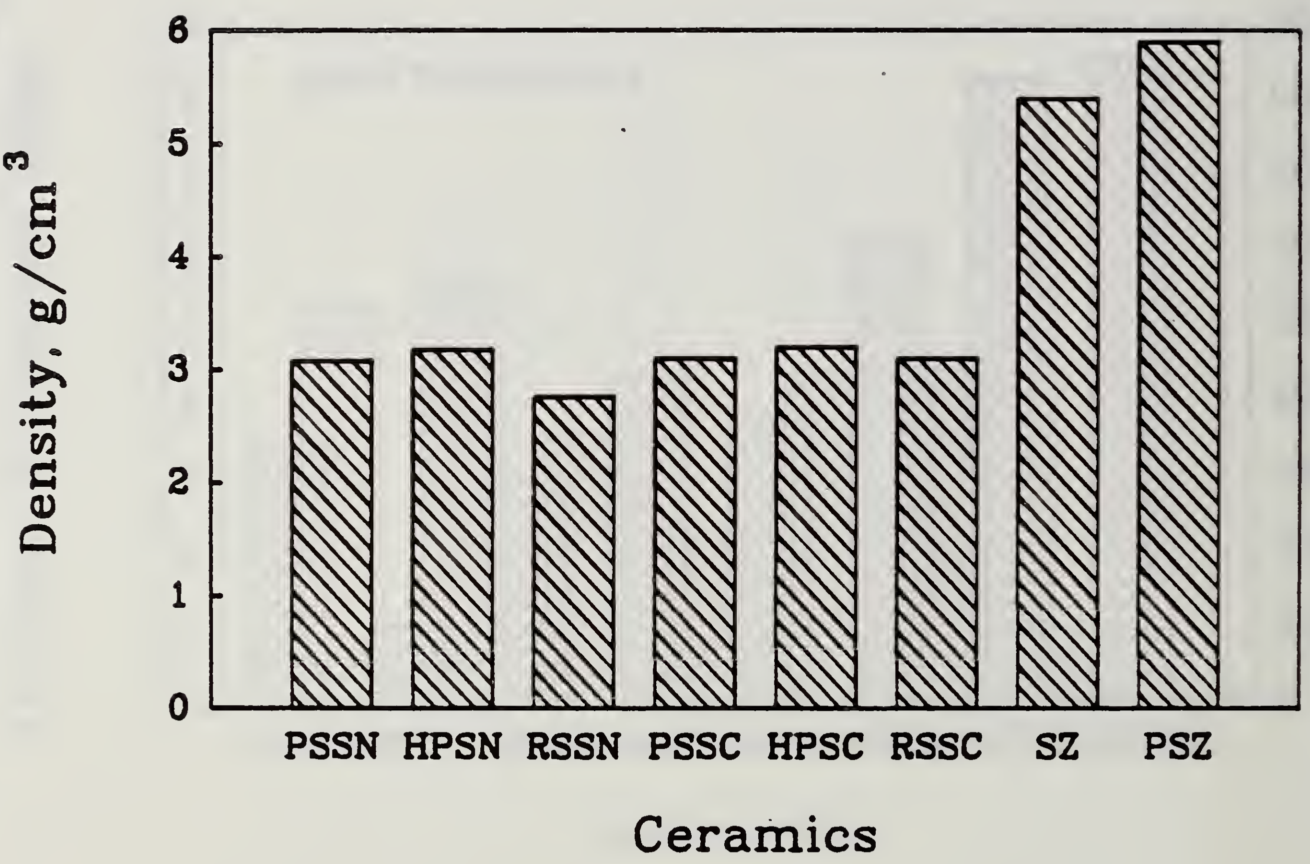


Fig. 12: Linear thermal expansion coefficient of selected ceramics

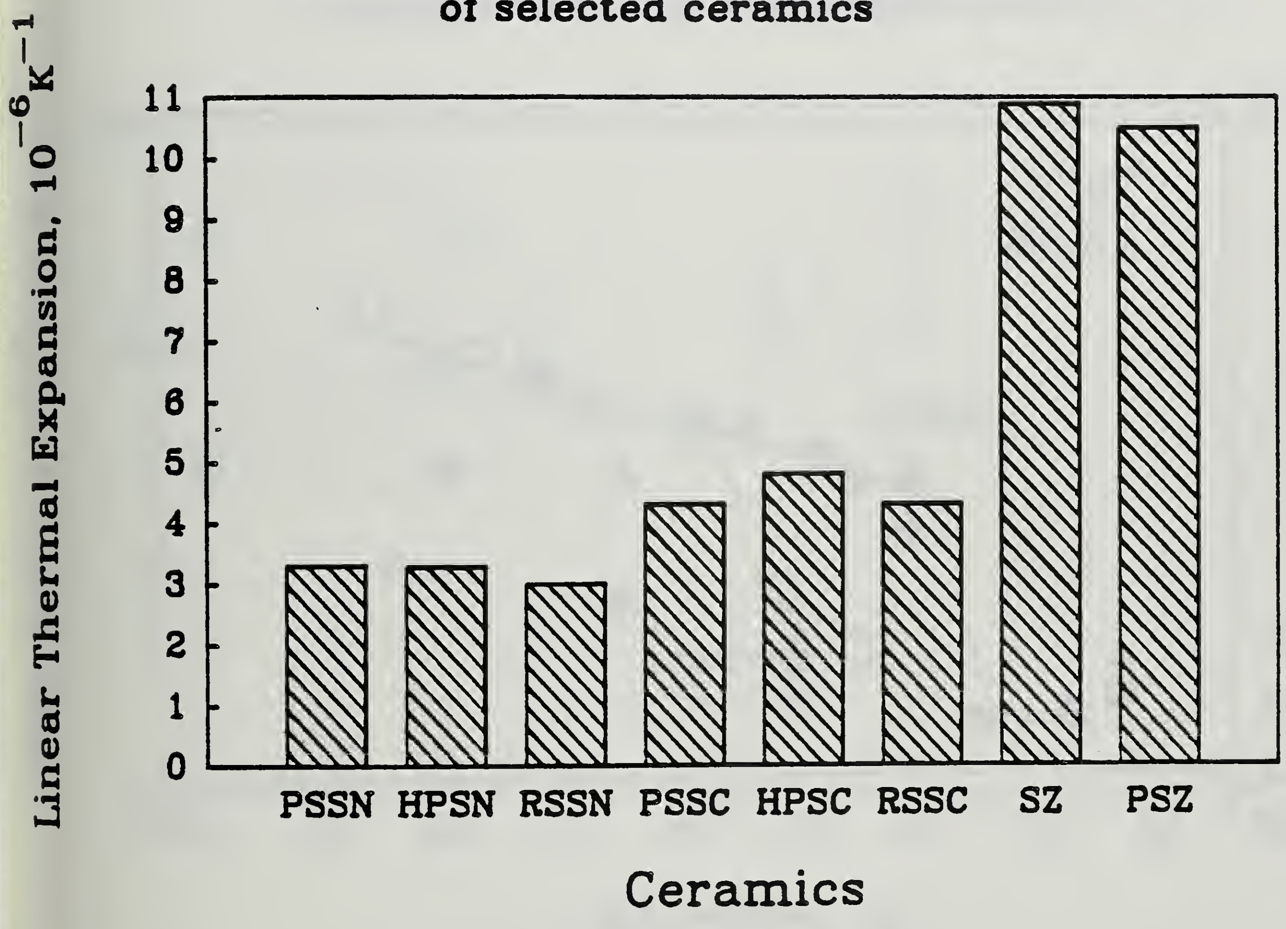


Fig. 13: Wear as a function of load for different batches of alumina

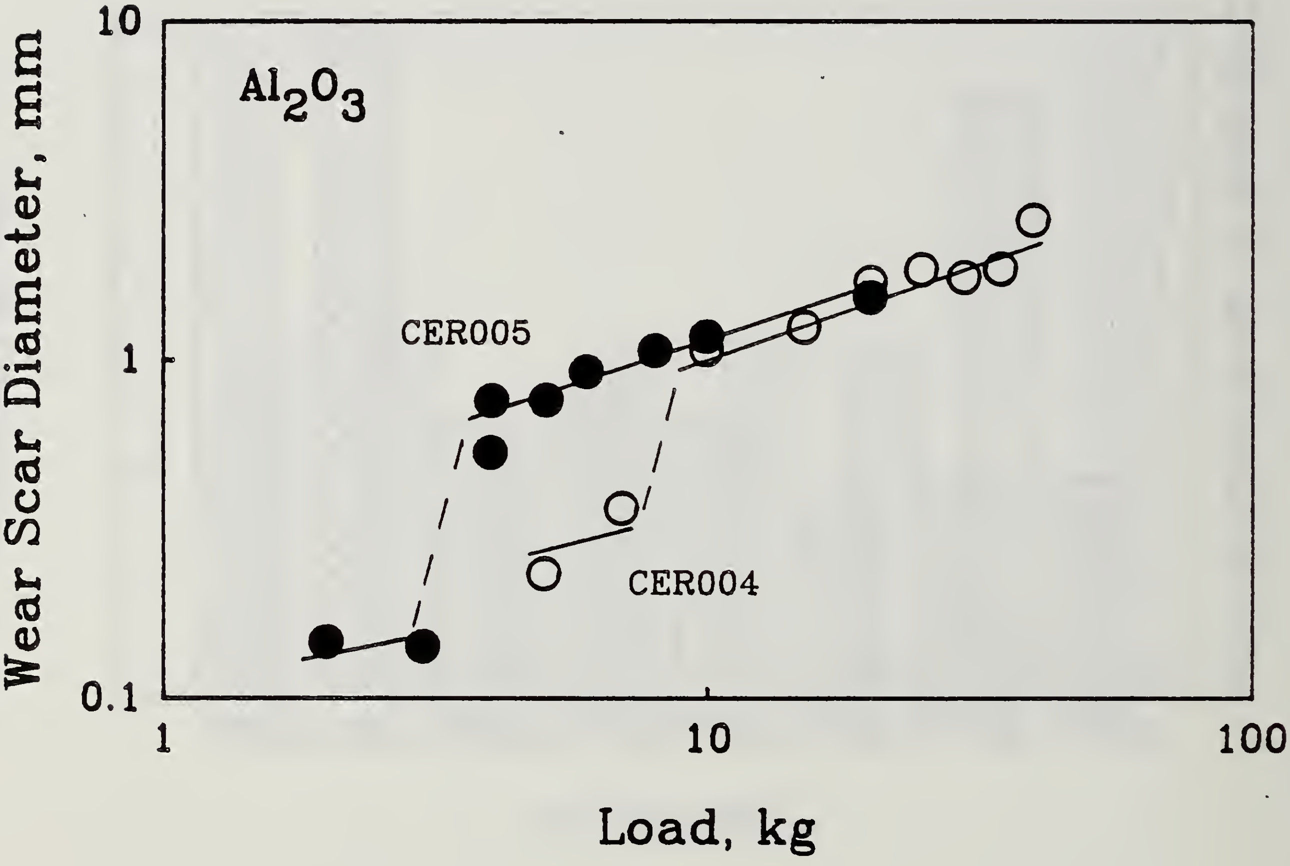


Fig. 14: Wear rate of silicon nitride as a function of humidity

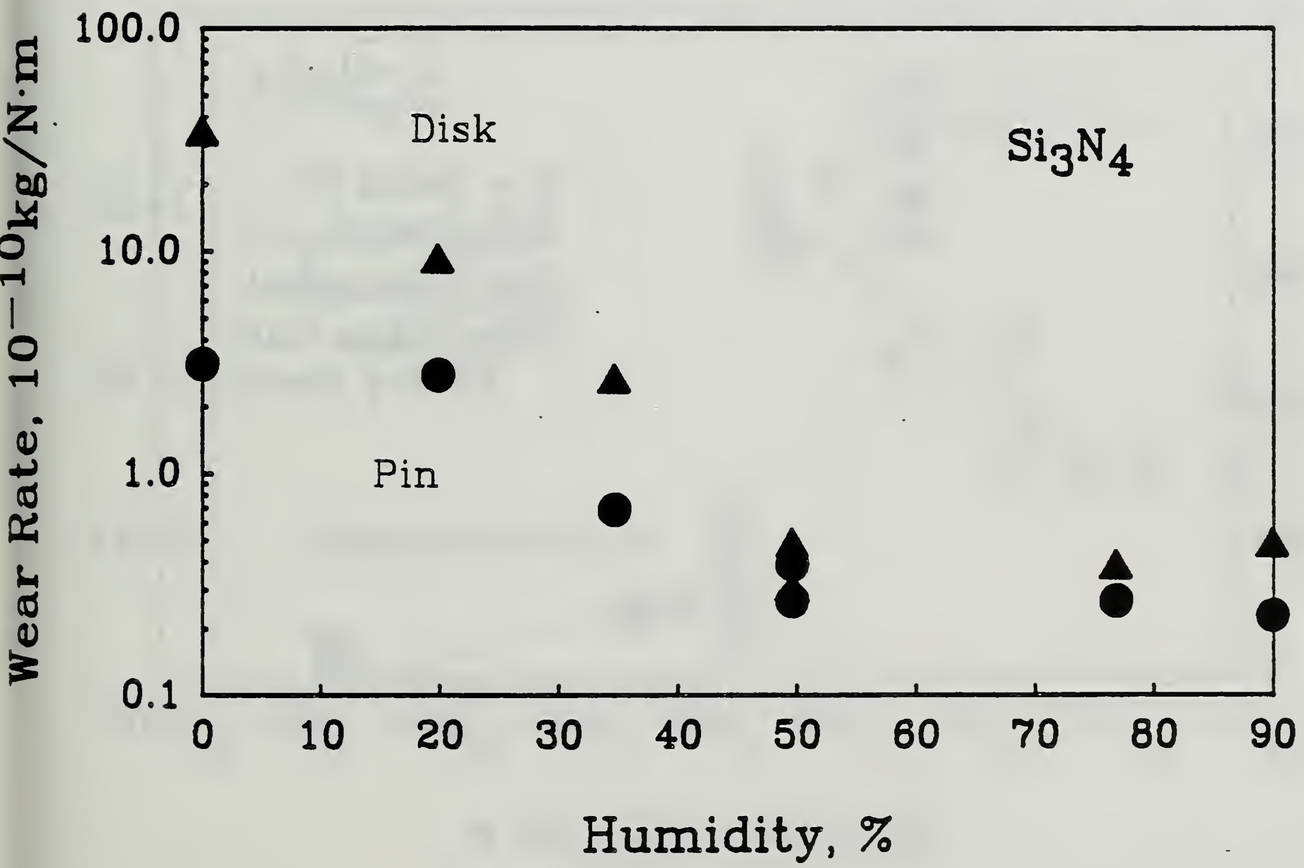


Fig. 15: Rate of wear of alumina as a function of slide direction on the basal sheets.

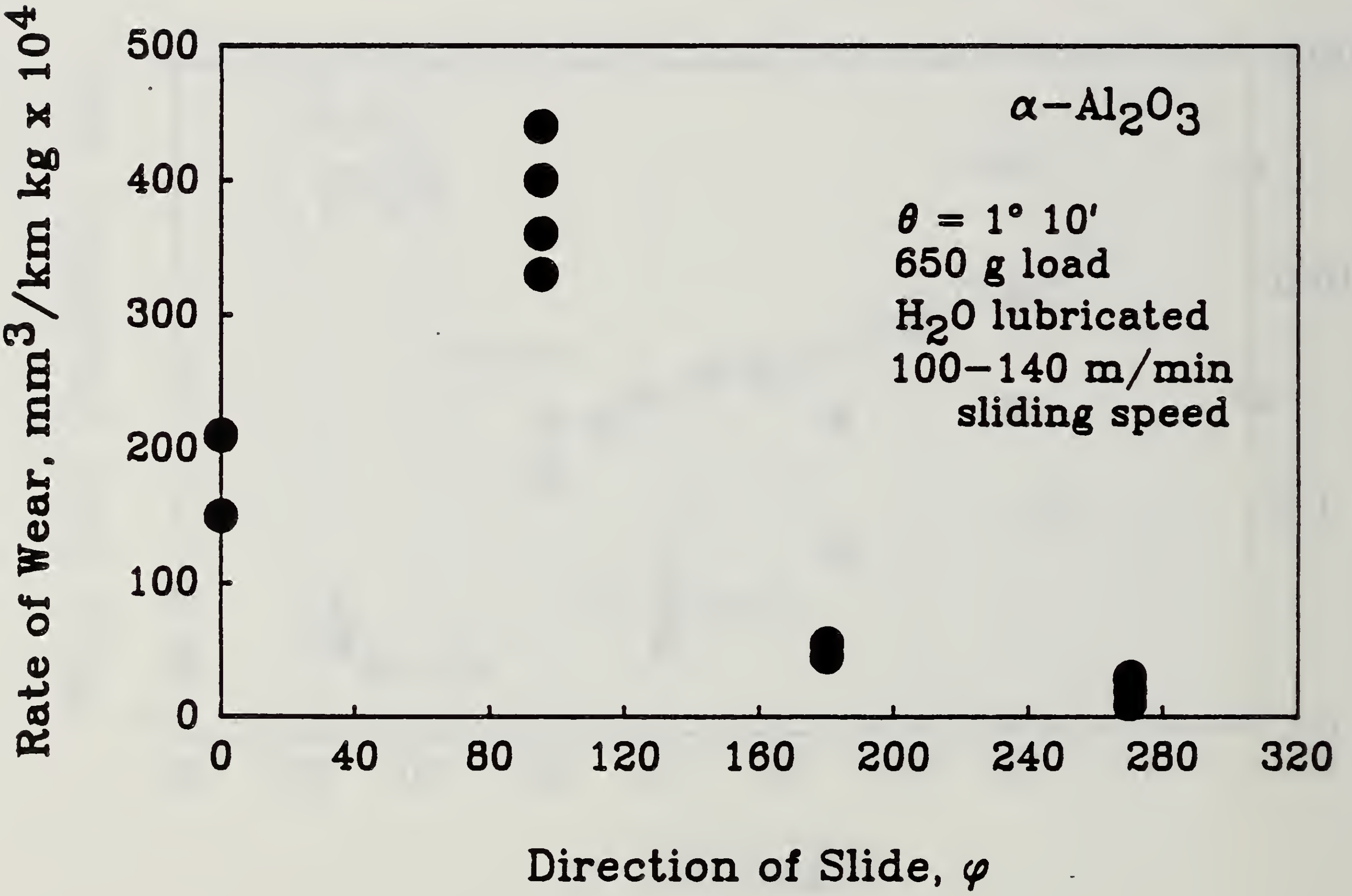


Fig. 16: Anisotropy in the wear of alumina.

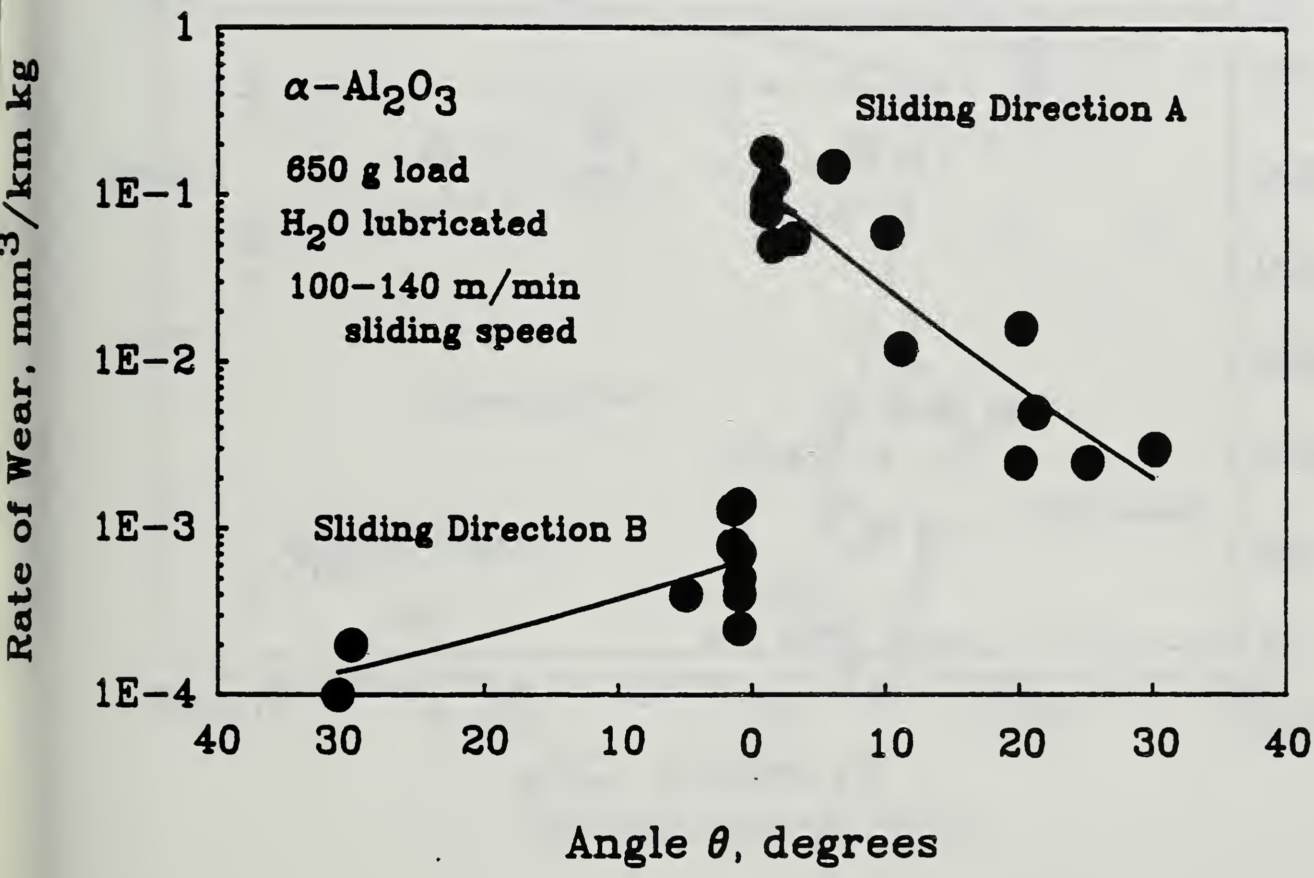


Fig. 17: Phase diagram of zirconia

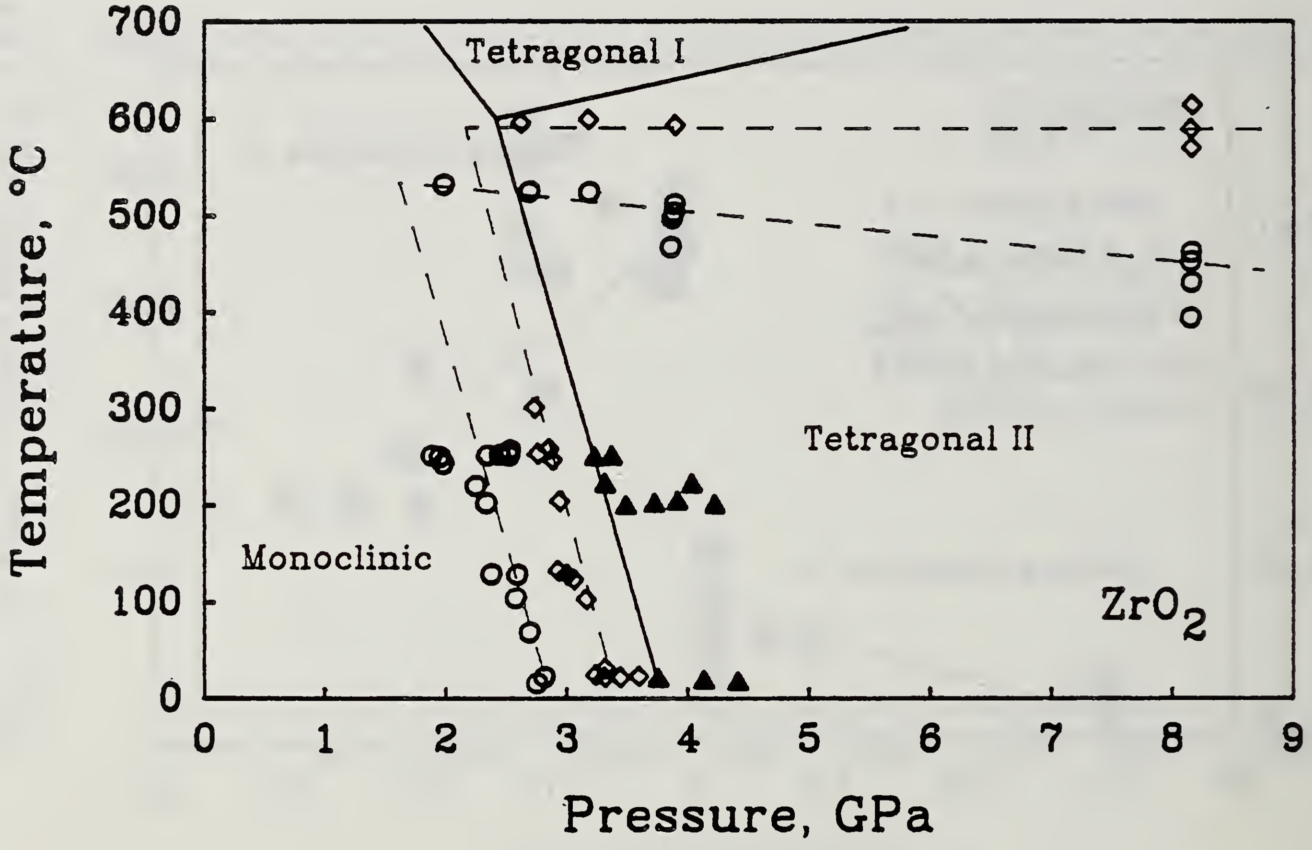


Fig. 18: Wear coefficients of alumina derived from literature values

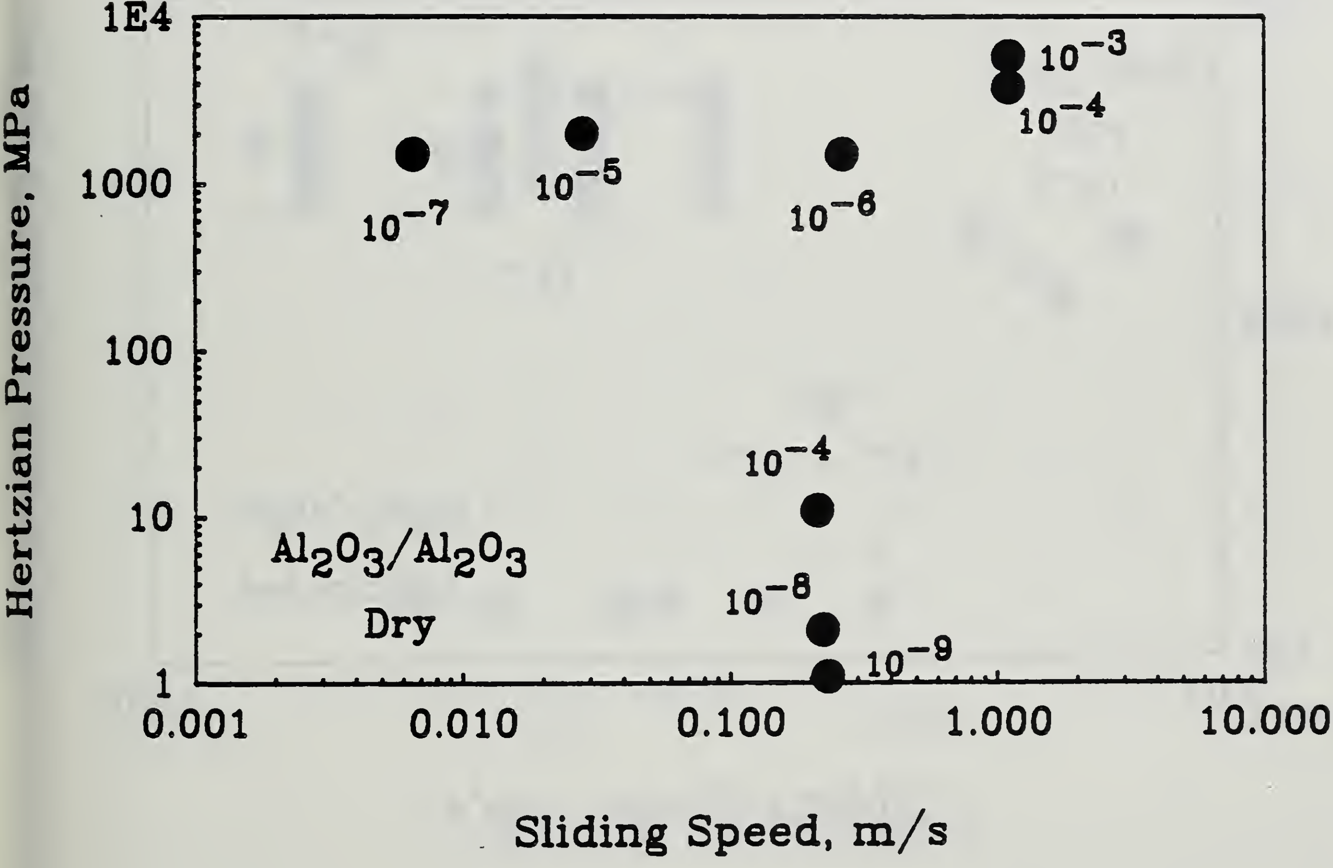


Fig. 19: Wear coefficient of lubricated alumina derived from literature results.

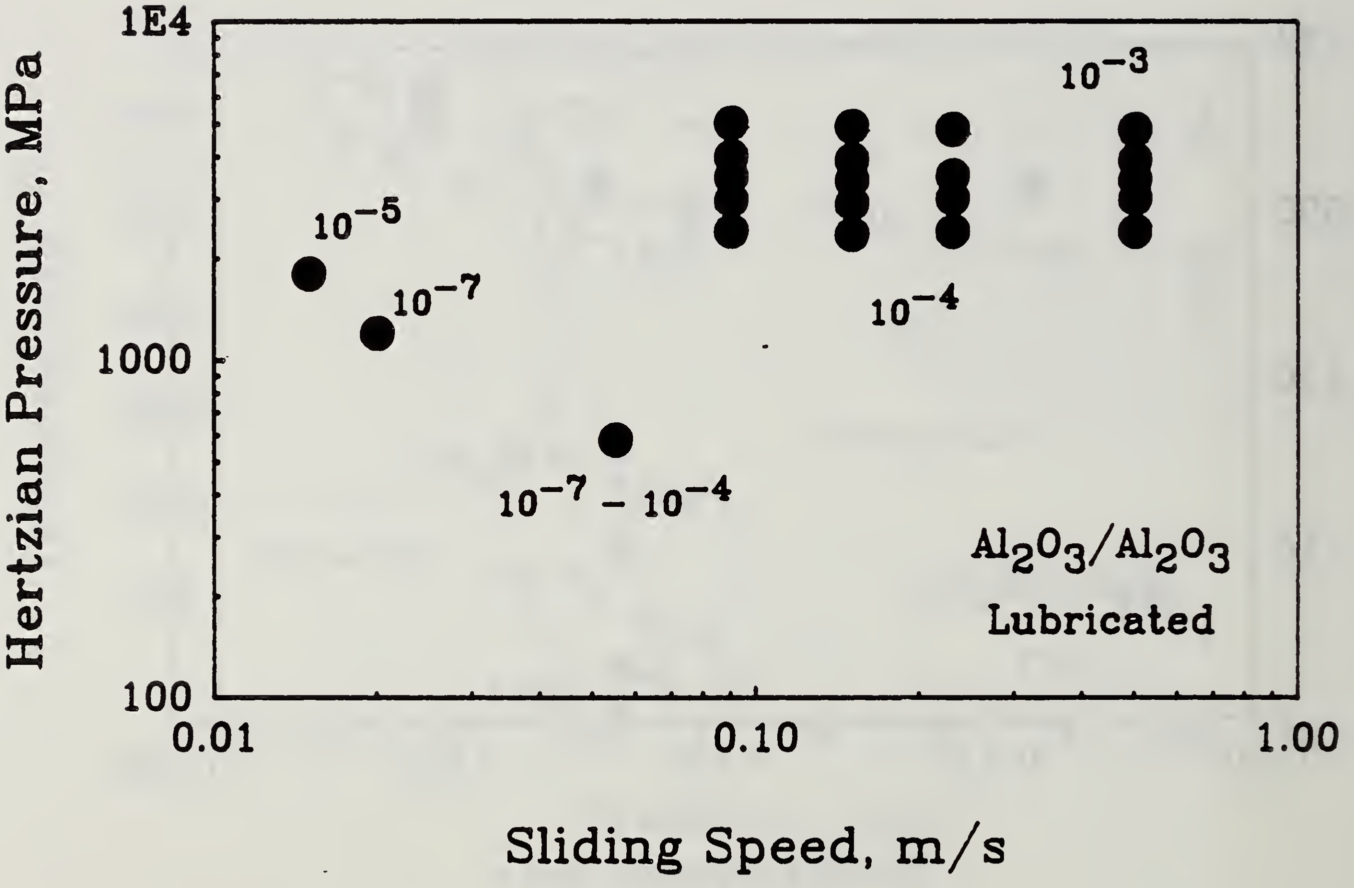


Fig. 20: Wear coefficient of silicon nitride derived from literature results.

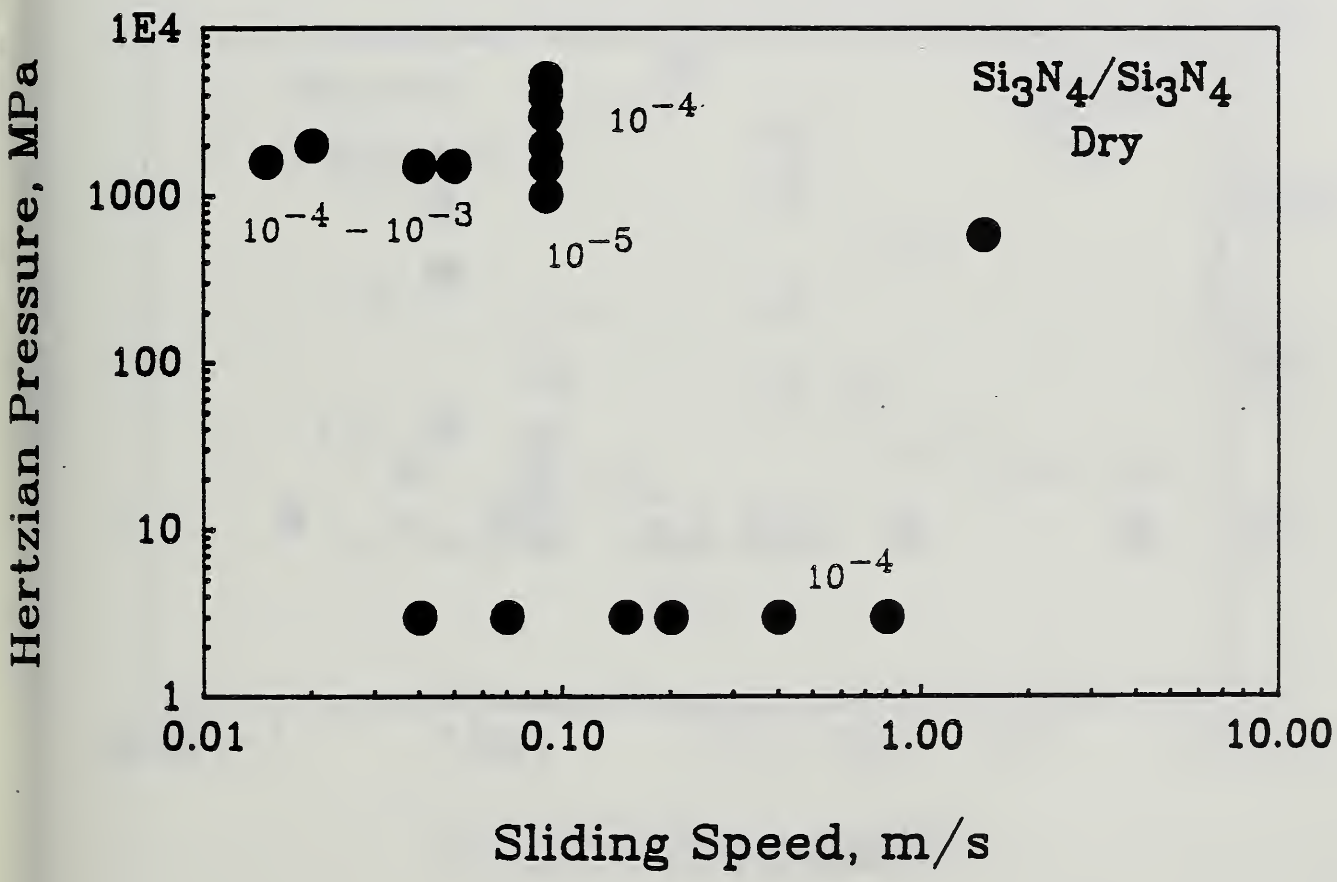


Fig. 21: Wear coefficient of silicon carbide derived from literture results.

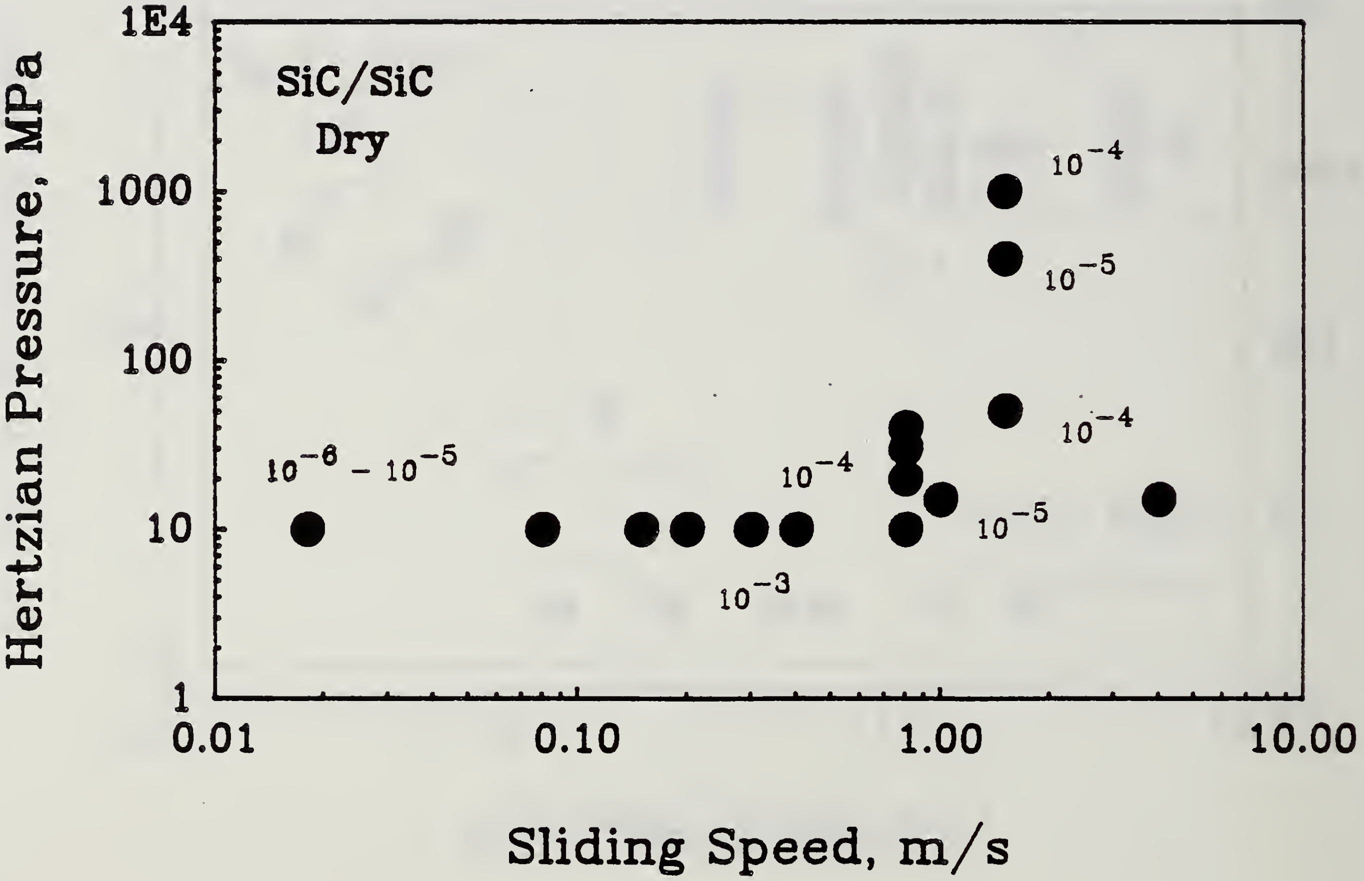


Fig. 22: Wear coefficient of partiallly stabilized zirconia derived from literature results.

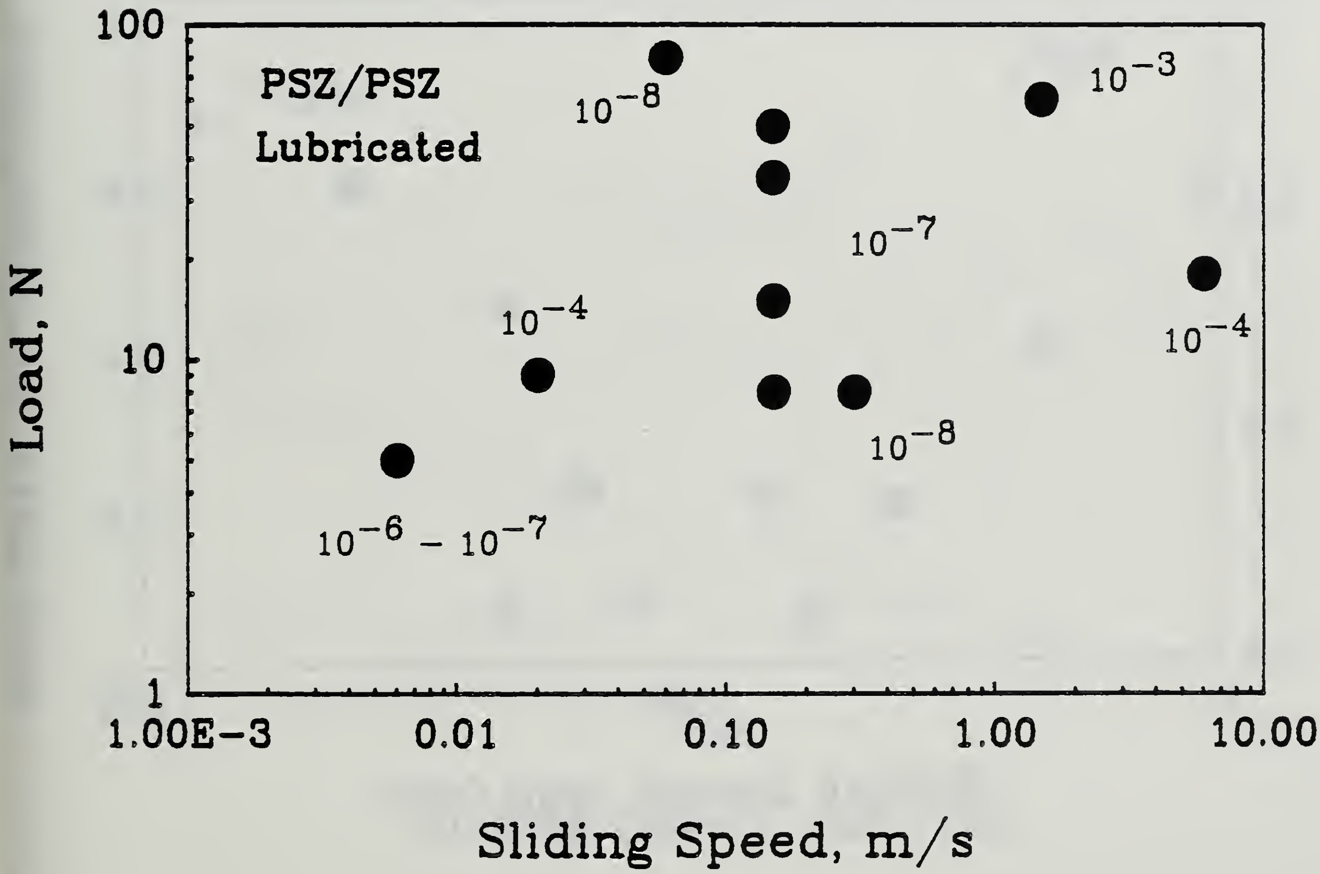


Fig. 23: Coefficient of friction of silicon nitride as a function of sliding speed

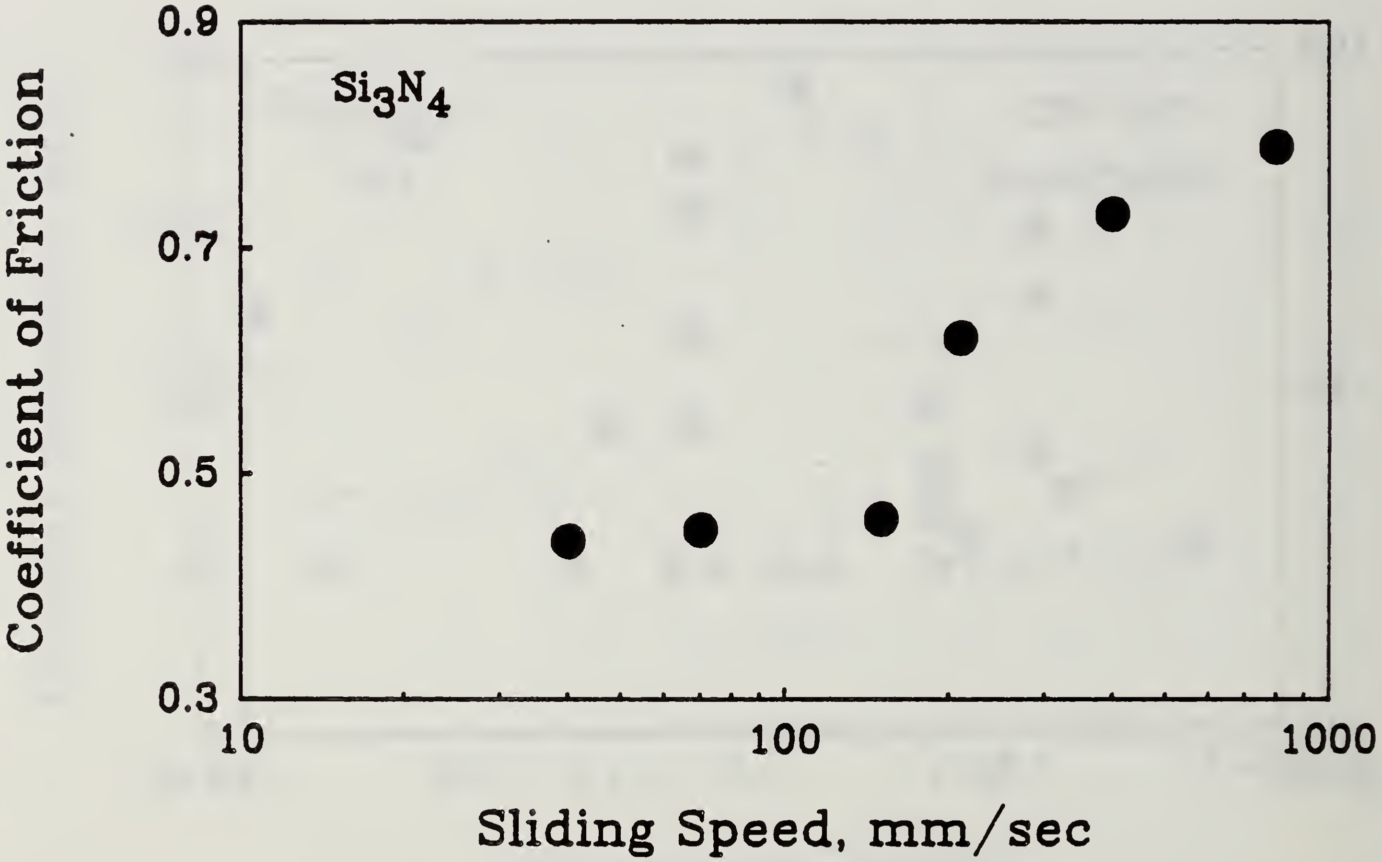


Fig. 24: Wear rate of silicon nitride as a function of sliding speed

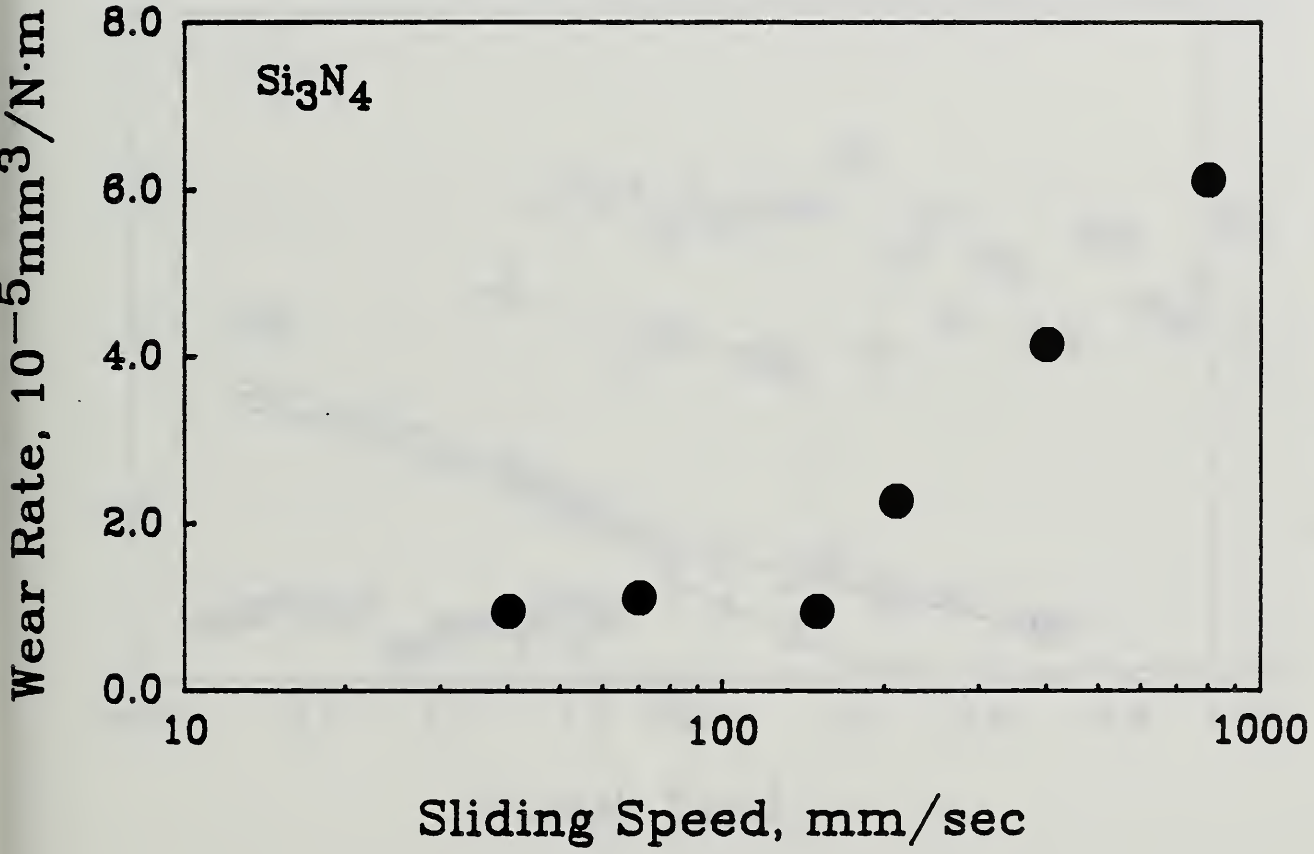


Fig. 25: A study of the dependence of wear transitions on material

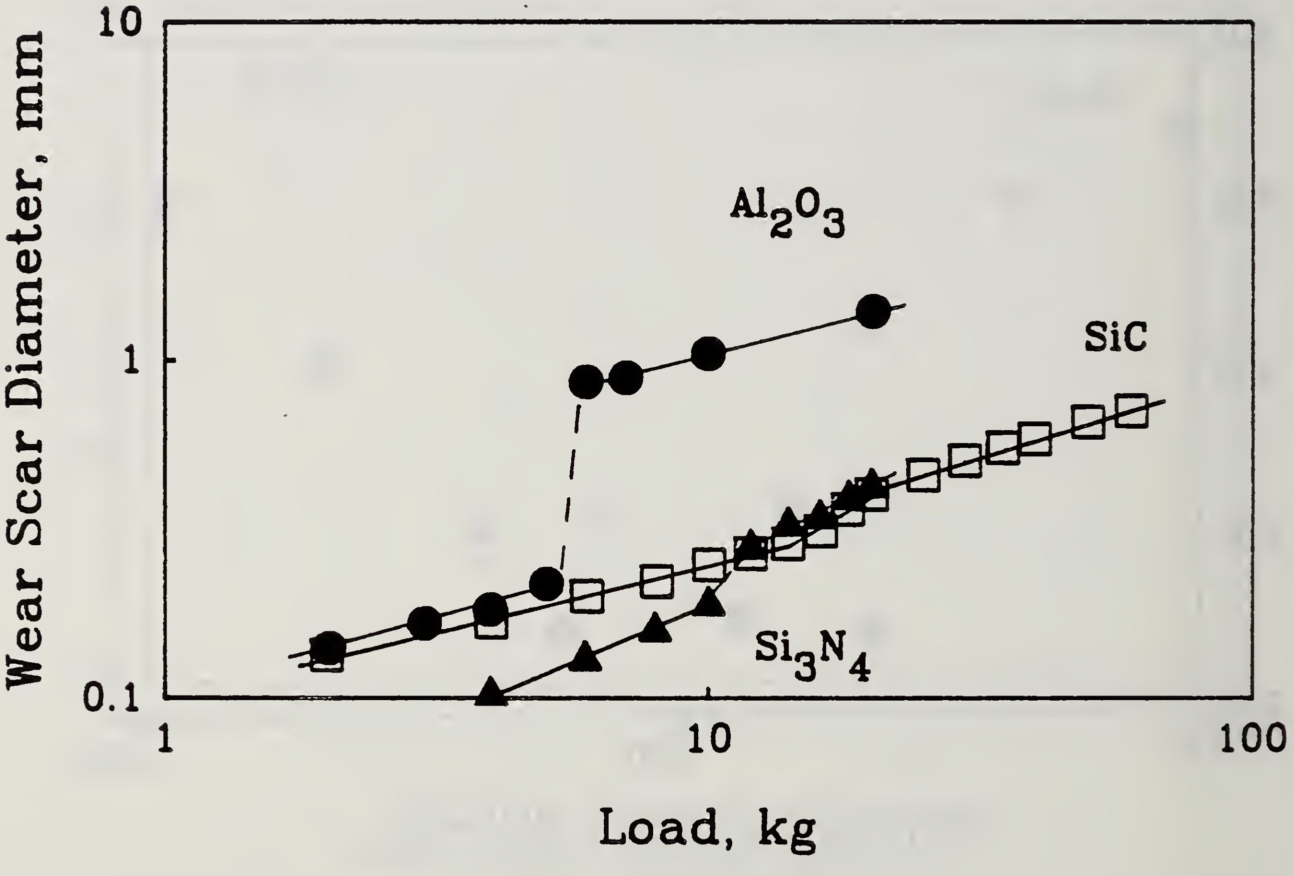


Fig. 26: Coefficient of friction of silicon nitride as a function of sliding distance

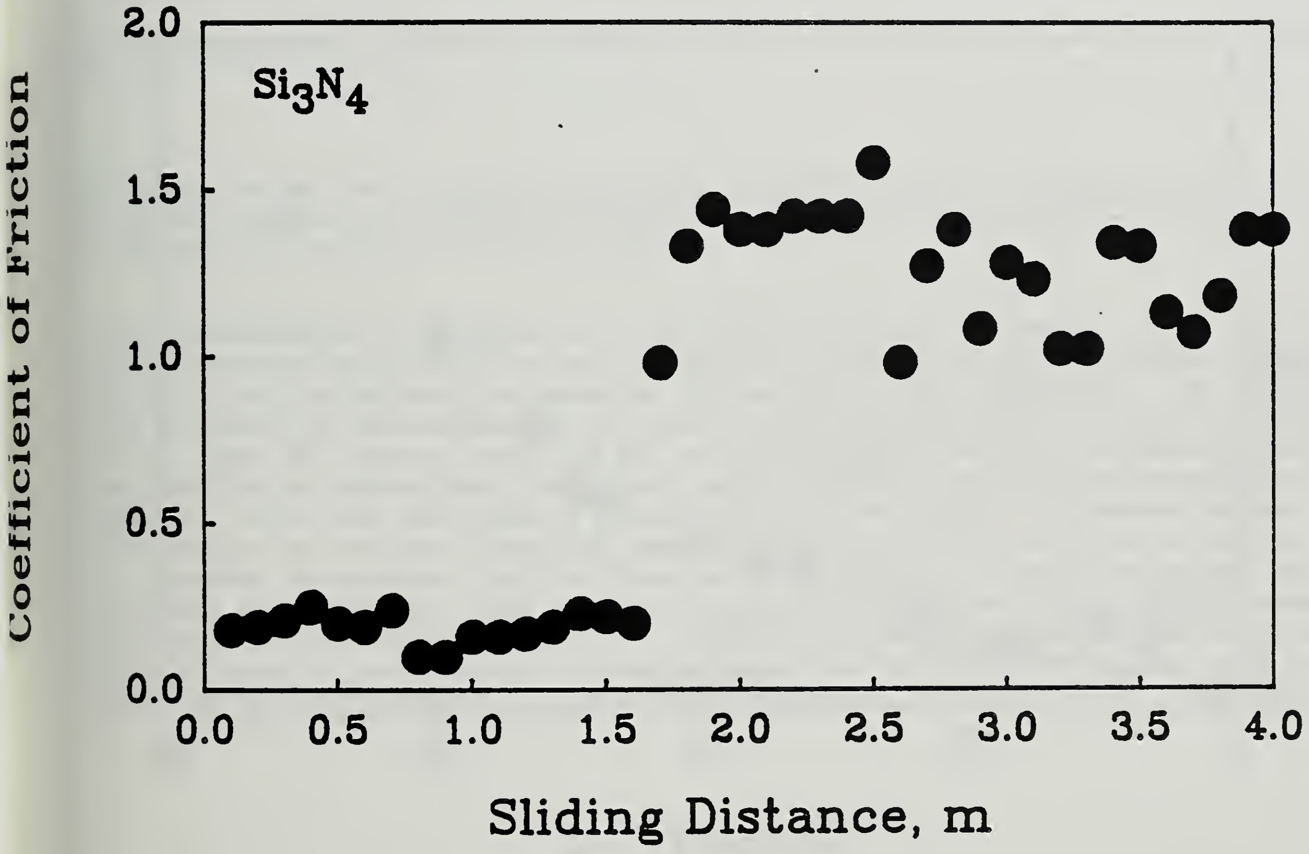
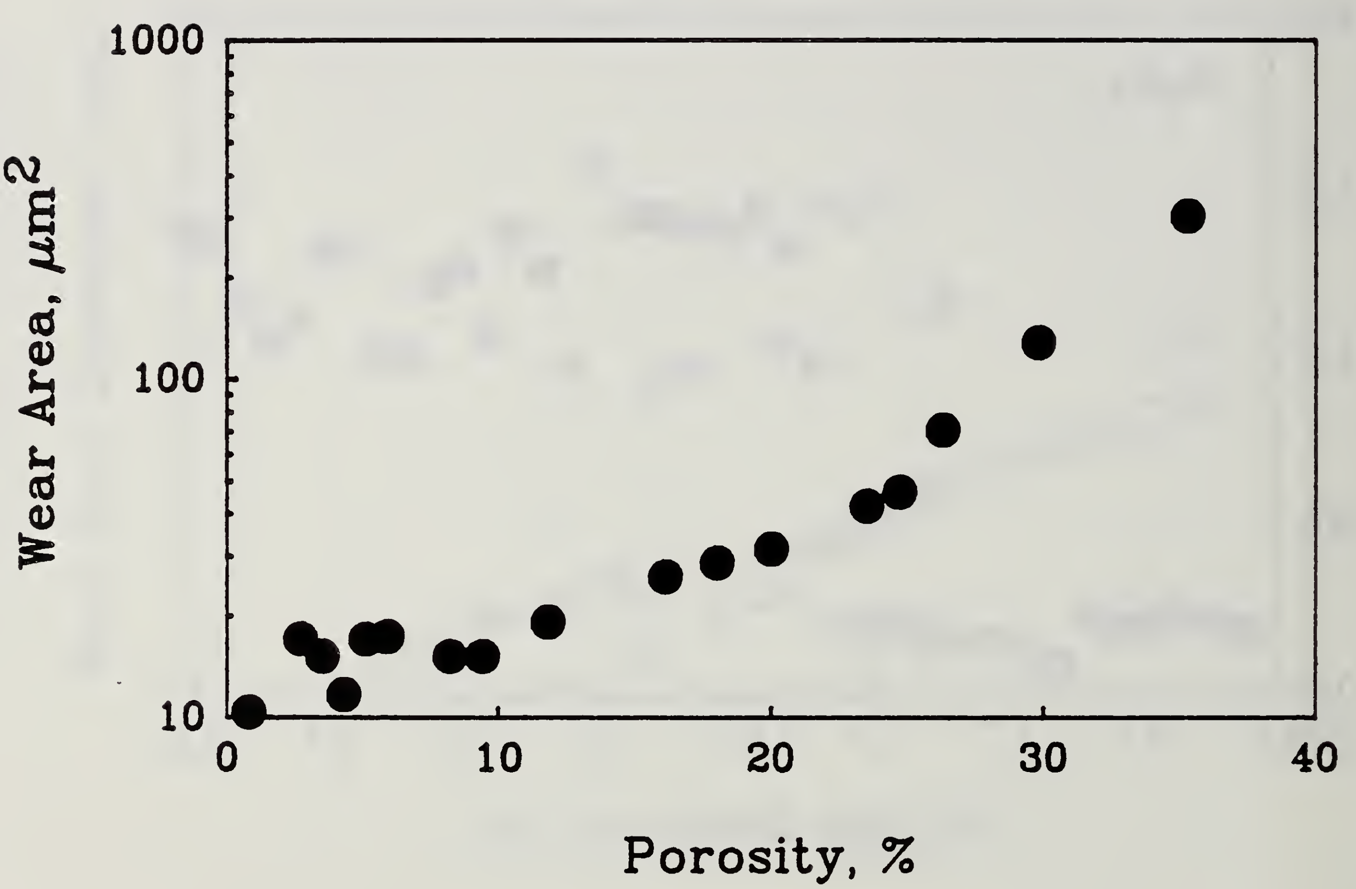


Fig. 27: Effect of porosity on the wear of alumina



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A critical assessment of the state of the art of the tribology of ceramics is made. To identify the critical technical barriers confronting the utilization of advanced gas-fired engines, data were gathered specifically on the tribology of materials for gas-fired engine applications. Site visits and discussions with a number of GRI contractors in industry were conducted as the first step in identifying critical issues. Then, an extensive review of the technical literature was made to determine what information was available to resolve those issues, and, more importantly, what critical information was not yet available. These data were used to examine the issues for each of the principal engine types (rotary, reciprocating, and turbine). Materials property data for ceramics were then reviewed in the context of the operating environments and conditions for these engines. Thermal, mechanical, and tribological properties were examined, along with the important considerations for lubricating ceramics in engine applications. The analysis of these data considered the impact and relative merits of using various advanced materials and resulted in recommendations for research activities that could have a significant impact on the development of gas-fired prime movers.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

assessment; gas-fired; natural gas; prime mover; tribology

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