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MATERIALS REVIEW FOR IMPROVED AUTOMOTIVE GAS TURBINE ENGINE — FINAL REPORT

C. Belleau, W. L. Ehlers, and F. A. Hagen
Chrysler Corporation

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U.S. DEPARTMENT OF ENERGY
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Division of Transportation Energy Conservation

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Abstract

Advanced materials are the key to achieving the performance and fuel economy goals of improved automotive gas turbine engines. The potential role of superalloys, refractory alloys, and ceramics in the hottest sections of future engines that may be required to operate with turbine inlet temperatures as high as 1370° C (2500°F) is examined. In this report, these high temperature materials are reviewed in three separate sections.

Superalloys

The characteristics of the best modern conventional superalloys, directionally solidified eutectics, oxide dispersion strengthened alloys, and tungsten fiber reinforced superalloys are reviewed; and the most promising alloys in each system are compared on the basis of maximum turbine blade temperature capability. The requirements for improved high temperature protective coatings and special fabrication techniques for these advanced alloys are discussed.

Refractory Alloys

Chromium, columbium, molybdenum, tantalum, and tungsten alloys are reviewed. On the basis of properties, cost, availability, and strategic importance, molybdenum alloys are found to be the most suitable refractory material for turbine wheels for mass produced engines.

Ceramics

Ceramic material candidates are reviewed and ranked according to their probability of success in particular applications. Various forms of, and fabrication processes for both silicon nitride and silicon carbide, along with SiAlON's are investigated for use in high-stress and medium-stress high temperature environments. Low-stress glass-ceramic regenerator materials are also investigated. Treatment is given to processing requirements, such as coatings for oxidation/corrosion protection, joining methods, and machining technology. Economics of ceramic raw materials, and of various processing methods are discussed. Conclusions are drawn, and recommendations for areas of further research are proposed for consideration and/or adoption.

Foreword

This "state-of-the-art" review of advanced materials for use in the hot zone of an Improved Automotive Gas Turbine (IGT) Engine, was prepared by the High Temperature Materials Research Department of Chrysler Corporation, as a supplement to the DOE/NASA Upgraded Gas Turbine Engine Program, Contract No. EY-76-C-02-2749.A011.

The engine development program, which is currently sponsored by the Heat Engine Systems Branch, Division of Transportation Energy Conservation of the Department of Energy (DOE), began in 1972 under the Environmental Protection Agency (EPA) as a demonstration of the low emissions potential of the automotive gas turbine. Using Chrysler's sixth generation 150 HP gas turbine as the Baseline engine, a component improvement program was structured of tasks to improve emissions control and reduce engine cost. A major change in the program took place during the period of the 1973-1974 energy crisis. Contract administration was transferred to the newly formed Energy Research and Development Administration (ERDA), and a goal to demonstrate potential for good fuel economy was added.

A study to assess the potential for developing an IGT propulsion system was implemented as an add on task to the Upgraded Engine Program (see Vol. 3 - Final Report).

A specific goal of the study was to design a pre-prototype engine which would be capable of a 20% fuel economy improvement over that of a conventional (1983) automotive spark ignited piston engine. This advanced turbine engine must also have comparable performance, reliability, and potential manufacturing cost. It is generally recognized that the key to the achievement of the program goals is a significantly higher turbine inlet temperature (TIT), possibly as high as 1370°C (2500°F) However, even a relatively modest increase over the 1050°C (1925°F) TIT of the current Upgraded turbine engine would probably result in material temperatures beyond the capabilities of the best conventional superalloys.

Since it was apparant that the high temperature properties of available materials of construction would, to a large extent, determine the design limits of the IGT, an extensive study of high temperature turbine materials technologies was initiated. In this study three pertinent material categories are considered. 1. superalloys, 2. refractory metals, and 3. ceramics, and their current state-of-the-art is identified. Advantages and disadvantages of the various materials, their processing requirements, as well as their economic considerations are outlined. Conclusions and recommendations are drawn.

The Chrysler program is managed and coordinated by the Research Section of the Engineering Office. Mr. C. E. Wagner - Senior Research Staff Engineer, is the Program Manager. The technical monitoring agency for the program is the Gas Turbine Project Office of the National Aeronautics and Space Administration (NASA), at the Lewis Research Center, Cleveland, Ohio. Mr. Paul T. Kerwin serves as the NASA Project Officer.

The authors thank Mr. J. H. Engel, Jr., Manager High Temperature Materials Research, and Mr. J. M. Corwin, Senior Research Staff Scientist, for their helpful comments and criticisms throughout the writing of this review. This study was performed during the period January, 1977 through March, 1978, the final report being submitted in April, 1978.

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April, 1978

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Executive Summary

This report, a supplement to a DOE/NASA-Sponsored Automotive Gas Turbine Engine Development Program (DOE Contract No. EY-76-C-02-2749.A011), reviews the state of the art of advanced high temperature materials for possible application in the hot zone of an Improved Gas Turbine (IGT). To achieve the higher levels of performance and fuel economy of an IGT, it is generally recognized that significantly increased turbine inlet temperatures (TIT) will be required.

Even a relatively modest increase over the 1050°C (1925°F) TIT of the current DOE/NASA Upgraded Engine would require material properties beyond the capabilities of the best conventional superalloys. The potential role of advanced superalloys, refractory alloys, and ceramics in IGT's that may be required to operate with TIT's as high as 1370°C (2500°F) is examined. In this report, these advanced high temperature materials are reviewed in three separate sections.

Superalloys

Conventional superalloys, directionally solidified eutectics (DSE), oxide dispersion strengthened alloys (ODS) and tungsten fiber-reinforced superalloys were reviewed and compared on the basis of "turbine blade temperature capability". For this study, temperature capability was arbitrarily defined as the temperature to produce rupture at 138 MN/m^2 (20 KSI) in 1000 hours.

Today's best conventional cast superalloys are limited to an uncooled blade temperature of about 980°C (1800°F). Even with continued development and advanced processing techniques, such as directional solidification, this temperature will probably not be extended more than about 25°C (45°F). Wrought superalloys prepared by the usual forging or powder metallurgy techniques do not generally attain the strength of cast alloys in this temperature range.

Significant increases in high temperature properties have been attained by applying the directionality concept to eutectic systems and tungsten fiber superalloy composites. Directionally solidified eutectics offer the possiblity of blade temperatures 60-110°C (110-200°F) above those used for conventional cast superalloys. Although tungsten fiber reinforced superalloys afford potentially the highest use temperature capability of any of the superalloy-base systems studied for turbine blades, i e. about 1200°C (2200°F), their application, because of cost and fabrication problems, is most remote.

Advanced oxide dispersion strengthened alloys with elongated or fibrous grain structures appear to have a potential-use temperature of about 1040°C (1900°F) for blades and up to 1230°C (2250°F) for lower stressed stator vanes Recently, wrought alloys produced from powder prepared by a new rapid solidification rate process (RSR) have been reported (P & WA) that appear to have the potential of increasing the maximum temperature capability of conventional superalloys by about 50-100°C (90-180°F).

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With the notable exception of some of the ODS alloys containing both chromium and aluminum, almost all of the advanced superalloy systems mentioned have relatively poor oxidation resistance and will probably require protective coatings at temperatures above about 1000°C (1830°F). The standard aluminide diffusion coatings provide long term protection only up to about 1040-1100°C (1900°-2000°F). Newer, more costly overlay coatings may extend this range to around 1150°C (2100°F)

Before the advanced superalloy-base materials studied in this report could be considered for a practical small automotive-size turbine rotor, many serious cost, design and fabrication problems would have to be solved. A near net shape integral rotor appears to be necessary to avoid the intolerably high fabrication and assembly costs associated with the individual blade-type construction commonly used for larger aircraft-type turbine rotors. Two processes, investment casting and isothermal superplastic forging, have the potential to produce relatively low-cost integrally bladed turbine rotors

Politically generated uncertainties in the supply of key alloying elements, particularly chromium, and rapidly rising prices cloud the future for any large scale usage of superalloys in automotive gas turbines.

Refractory Alloys

Five refractory metals — chromium, columbium, molybdenum, tantalum and tungsten and their alloys were examined. Some of the alloys appeared to offer usable properties for turbine rotor application at temperatures well over 1150°C (2100°F). However, they all have undesirable features that detract from their potential usefulness and final selection would, at best, be a compromise.

While tantalum and tungsten have more than adequate stress-rupture strength, their high density would impose unreasonable inertia penalties when used in rotating components. Chromium alloys, on the other hand, would be quite advantageous from the same standpoint, having a lower density than nickel-base alloys, but their extreme brittleness and sensitivity to interstitials preclude their use for such an application. From the standpoint of frabricability many refractory alloys perform rather poorly. Chromium and tungsten base alloys (Group VI A) because of their low ductility are difficult to reduce mechanically to usable products. Chromium in particular requires extrusion or swaging to gross final shape. Tantalum and columbium on the other hand are very ductile (Group V A) and are readily fabricable although requiring high deformation forces. Molybdenum, while in Group VI A, has intermediate fabricability. Tantalum and tungsten because of their extremely high melting points, have not been successfully investment cast.

Although alloys of both columbium and molybdenum are normally used in the wrought condition, several of them have recently been investment cast with extremely encouraging results. The experimental shapes produced included small integral turbine rotors and commercial engine size airfoil shapes with acceptable surface finish. In view of the small size of the projected turbine rotor, precision investment casting to net shape appears to be the only currently practical method of secondary fabrication.

In the event that the final material choice for the hot gas path components of the IGT is a refractory alloy, raw material cost will be an important consideration in mass production decisions. While the relatively low cost of chromium is undoubtedly attractive, some alloy development breakthroughs are required before full advantage can be derived from that alloy system. At the other end of the scale the high cost of tantalum coupled with a high density precludes serious consideration of its use as a compressor-turbine rotor material. Tungsten-base alloys are of intermediate cost but have a high ductile-to-brittle transition temperature.

The base materials for the castable refractory alloys, columbium and molybdenum, are practically at opposite ends of the cost range, with molybdenum second only to chromium. This cost advantage holds not only for the pure metal but also for the commercial alloys which contain less than 2% additions. Availability and strategic importance, while not the primary selection criteria, strongly favor molybdenum in view of its ample domestic reserves and production capacity.

The stress-rupture properties of the various molybdenum and columbium alloys cover essentially the same range and the selection is usually governed by fabricability. In a cast turbine rotor, where property optimization by thermo-mechanical treatments is not feasible, the actual properties are expected to be in the range of recrystallized or stress-relieved alloys and will be affected by process variables. The properties of the cast columbium alloys are reported to be comparable to that of the wrought material (with similar thermal history); actual test results show cast molybdenum-base TZM alloy to be somewhat superior to the stress-relieved wrought alloy.

The creep properties of molybdenum alloy TZM, cast and wrought, are also superior to that of the strongest columbium alloys. While molybdenum alloys appear to be the best suited of the refractory alloys for the rotor of a high-temperature turbine, they have one common serious deficiency; a catastrophic oxidation behavior. In spite of that problem they remain extremely attractive because of their unique hot strength. The oxidation is partially alleviated by the use of protective coatings. However, serious consideration of the usage of molybdenum alloys in the IGT would require additional development efforts particularly in the area of coating reliability.

The use of refractory metals can be summarized as follows. While tantalum and tungsten have more than adequate stress-rupture strength, their high density would impose unreasonable inertia penalties when used in rotating components. Chromium alloys, on the other hand, would be quite advantageous from the same standpoint, having a lower density than nickel-based alloys, but their extreme brittleness and sensitivity to interstitials preclude their use for such an application. From the standpoint of fabricability, many refractory alloys perform rather poorly. Chromium and tungsten base alloys (Group VI A), because of their low ductility, are difficult to reduce mechanically to usable products. Chromium in particular requires extrusion or swaging to gross final shape. Tantalum and columbium, on the other hand, are very ductile (Group VI A) and are readily fabricable, although requiring high deformation forces Molybdenum, while being in Group VI A, has intermediate fabricability. Tantalum and tungsten, because of their extremely high melting points, have not been successfully investment cast.

Ceramic Materials

It is clear that substantial increase in fuel efficiency in a gas turbine engine will be realized only if the turbine inlet temperature is increased significantly. Such temperatures could be well above those considered practical for the best available superalloys or with the refractory metals, generally because of poor oxidation resistance, undesirably high density, fabrication problems, high raw material cost, and uncertain availability.

The following ceramic materials, listed in order of greatest immediate potential, were reveiwed and compared for use at high-stress, high-temperature locations within a marketable gas turbine engine. It should be emphasized that none of the following have properties which have, to date, been completely optimized.

1. **Hot Isostatically Pressed Silicon Nitride -** offers the greatest potential for high strength and high Weibull Modulus at elevated temperatures, and, in principle, is capable of economical, high volume production of complex parts. Development, however, has been moving slowly.

2. **Sintered Alpha Silicon Carbide -** Exclusive to the Carborundrum Company, this material demonstrates no strength degradation through 1650°C (3000°F), and has unequaled oxidation resistance compared to any form of silicon carbide or silicon nitride It is capable of being formed to shape, although injection molding is not possible at this time on cross sections greater than 12.5 cm (0.5 in) because of binder bake out cracking

3. **Sinterable Silicon Nitride -** offers the potential for low cost, complex [illegible] fabrication, however high temperature strength, and oxidation resistance are limited, resulting from the addition of sintering aids to the Si_3N_4 powder

4. **Chemical Vapor Deposited Silicon Carbide -** Excellent potential for high strength and oxidation resistance; however very serious fabrication problems continue to hamper developmental progress.

5. **Sinterable Beta Silicon Carbine -** Although this material displays many of the fine properties of sintered Alpha SiC, there is no commercial source of beta SiC powder.

6. **Hot Pressed Silicon Nitride -** The strength of this material is exceptionally high at room temperature, falling off quite drastically by 1370°C (2500°F) The process remains prohibitively expensive and time consuming; therefore it does not lend itself to high volume production.

7. **Hot Pressed Silicon Carbide -** also prohibitively expensive for high volume production.

Materials considered as medium-stress candiates were 1) Recrystalized SiC, 2) Reaction sintered silicon carbide, 3) Reaction bonded silicon nitride, 4) Si Sic composites, and 5) SiAION For specialized applications, each differs in its potential for success Each has both benefits and disadvantages

Materials reviewed for regenerator recuperator application in order of greatest potential for success, were 1) AS (aluminum-silicate), 2) MAS/LAS (magnesium-alumino silicate lithium-alumino silicate) Pure MAS is subject to thermal fatigue, while pure LAS is subject to chemical attack by sulphur (in fuel) and road salt ingestion.

Coatings for oxidation/corrosion protection were reviewed and found to be unnecessary on those forms of SiC containing no free silicon. Forms of SiC containing free silicon readily oxidize at high temperature, however this may be considered protective rather than destructive. It is inconclusive as to whether a surface layer of pure CVD Si_3N_4 would benefit reaction bonded silicon nitride or hot pressed silicon nitride.

Joining methods for ceramics were reviewed and grouped into four major categories: 1) Adhesive and Cements, 2) Mechanical Bonding, 3) Solid Phase Joining, and 4) Liquid Phase Joining. Specialized applications of each were discussed.

Machining methods for ceramics were reviewed. Two methods were found most effective: 1) Diamond Machining, and 2) Ultrasonic Abrasive Machining. All methods of machining ceramics are expensive, and should be avoided by forming ceramic parts as close to design tolerances as possible.

Economics of ceramics, both in regard to raw material and processing, was investigated. Costs of raw materials are very low for SiC and Si_3N_4 when compared to superalloys or refractory metals, at least by an order of magnitude. Furthermore, such raw materials are in virtually unlimited supply in the United States. Processing costs and energy requirements are lower than for turbine metals, so long as final part machining is minimized. Although many economic variables are difficult to fully assess at this time, it is expected that ceramics would enjoy a cost advantage over the superalloys and the refractory metals if compared on a cost-per-part basis, owing to the lower bulk density of the ceramics.

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Section I

Superalloys

Section I - Superalloys

Introduction

Thermal efficiency and fuel economy requirements of the proposed high temperature Improved Automotive Gas Turbine engine (IAGT) dictate turbine inlet temperatures (TIT) possibly as high as 1310-1370°C (2400-2500°F). These extremely high temperatures combined with the special requirements of an economically feasible automotive turbine create major material problems that are significantly different from those encountered by aircraft turbines. Practical considerations such as cost, efficiency and size preclude the possibility of sophisticated cooling systems. Thus, airfoil components in the hot section would be expected to operate with actual metal temperatures approaching the TIT. Current problems in existing turbine engines associated with microstructural stability, surface stability and coatings would be greatly compounded by these higher temperatures.

Conventionally processed superalloys lose strength rapidly above 1100°C (2000°F). Without air cooling even the best superalloys do not come close to meeting the requirements for highly stressed components in the hot path of the proposed high temperature engines. It is apparent that a quantum jump in elevated temperature properties is needed. The only alternatives to current cast superalloys appear to be ceramics, refractory metals, and advanced superalloy-base composites. This first section will review in some detail the important superalloy-base composite materials that, because of their outstanding elevated temperature properties, might be considered for IAGT rotating hardware with greatly increased temperature capability and life expectancy. The three composite systems with the most potential are (1) directionally solidified (in-situ) eutectics, (2) oxide dispersion strengthened (ODS) alloys, and (3) refractory-wire reinforced (synthesized) composites.

This materials assessment will focus on the first stage turbine wheel as the critical component which largely determines the maximum temperature capability of the engine. Although first stage nozzle guide vanes operate where temperatures are higher, stresses are significantly lower than in rotating blades.

Turbine Blade Materials

Conventional Superalloys

In response to the needs of the aircraft gas turbine industry, concentrated and, more recently, quite sophisticated development efforts have now extended the use of nickel-base superalloys to the highest fraction of the base metal melting point of any common alloy system. Rather than striving to obtain the last 10°C to 20°C of maximum temperature capability* that may remain in this mature system, alloy developers in recent years have concentrated on improving some of the properties, other than tensile and creep-rupture strength, that affect the life of turbine blades, i.e. oxidation and hot corrosion resistance, ductility and impact strength, mechanical and thermal fatigue resistance, and structural stability.

The 100 hour and 1000 hour stress-rupture properties of the best cast superalloys such as MAR-M 246, MM 002, René 120, NASA TRW VIA, WAZ-20, and DS MAR-M 200 generally fall within the shaded bands shown in Figures I-1 and I-2. Directionally solidified eutectics, oxide dispersion strengthened alloys and refractory-wire composites are presented here and discussed later. When necessary, limited data were converted to 100 hour and/or 1000 hour stresses by utilizing the Larson-Miller parameter (Figure I-3). Best values were used wherever a choice was possible to show the maximum potential of an alloy or system. The nominal compositions of the conventional superalloys and the advanced composite materials are given in Table I-1.

The strength of conventional nickel-base superalloys drops off rapidly above 1100°C (2000°F). This occurs because the gamma prime (Ni_3Al) phase upon which these alloys primarily depend for high temperature strength tends to agglomerate or go into solution around this temperature. Another obvious limitation of this superalloy system is the incipient melting temperature which can occur as low as about 1200°C (2200°F) for the strongest, most highly alloyed compositions. One apparent way of achieving higher strength above 1100°C (2000°F) would be to select a nickel-alloy system with a melting point higher than that of current superalloys

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* *Temperature capability is often arbitrarily defined as the temperature for 1000 hour life in a 138 MN/m² (20 ksi) stress rupture test*

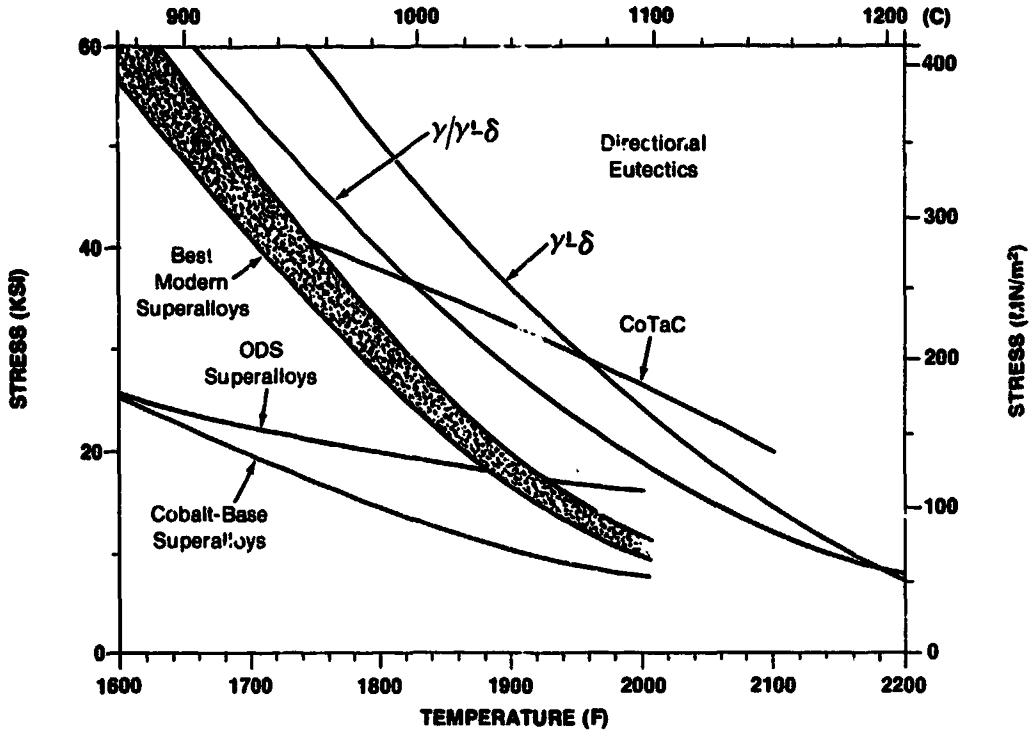

Figure I-1 100-Hour rupture strengths of conventional superalloys, ODS superalloys and directional eutectics.

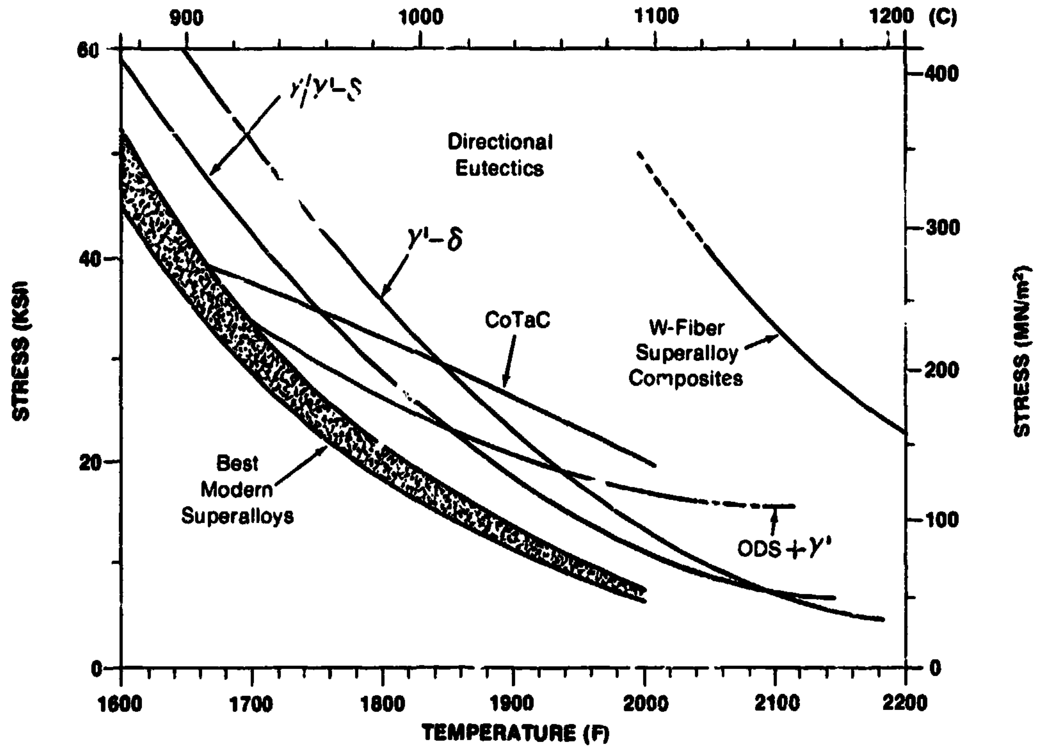

Figure I-2 1000-Hour rupture strengths of conventional superalloys, ODS+ gamma prime superalloys, directional eutectics and W-fiber composites.

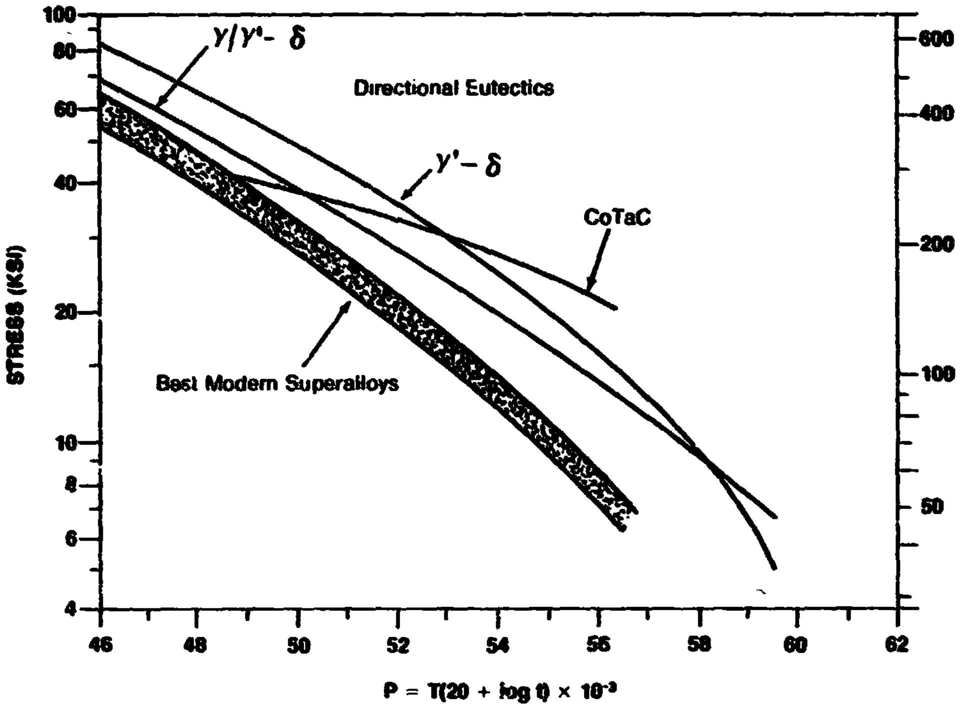

Figure I-3 Larson-Miller parameter stress-rupture curves for conventional superalloys and directional eutectics.

TABLE I-1
NOMINAL CHEMICAL COMPOSITION OF CURRENT AND ADVANCED SUPERALLOYS

Alloy Designation	Ni	Cr	Co	Mo	W	Cb	Ta	Al	Ti	C	Other*
MAR-M 200 (DS)	Bal.	9.0	10.0		12.0	1.0		5.0	2.0	0.13	
MAR-M 246	Bal.	9.0	10.0	2.5	10.0	—	1.5	5.5	1.5	0.15	
MAR-M 247 (MM 0011)	Bal.	8.3	10.0	0.7	10.0	—	2.0	5.5	1.0	0.15	1.5 Hf
MM 002	Bal.	9.0	10.0	—	10.0	—	2.5	5.5	1.5	0.15	1.5 Hf
MAR-M 509	10.0	23.5	Bal.	—	7.0	—	3.5	—	0.2	0.60	0.5 Zr
TRW-NASA (VIA)	Bal.	6.1	7.5	2.0	5.8	0.5	9.0	5.4	1.0	0.13	0.5 Re 0.4 Hf
WAZ-20	Bal.	—	—	—	20.0	—	—	6.5	—	0.20	
WAZ-D (ODS)	Bal.	—	—	—	16.6	—	—	7.3	—	0.05	1.3 Y_2O_3
MA-755E (ODS)	Bal	15.0	—	3.5	5.5	—	2.5	4.5	3.0	0.07	1.1 Y_2O_3
MA-956E (ODS)	—	20.0	—	—	—	—	—	4.5	0.5	0.05	0.5 Y_2O_3 Fe Bal.
MA 754 (ODS)	Bal.	19.0	—	—	—	—	—	0.3	0.4	0.05	0 [illegible] $_2O_3$
TD-Nickel (ODS)	Bal.	—	—	—	—	—	—	—	—	—	2.2 ThO_2
TD-Ni-Cr (ODS)	Bal.	21.0	—	—	—	—	—	—	—	0.1	2.0 ThO_2
Gamma prime-delta (DSE)	Bal.	—	—	—	—	23.1	—	4.4	—	—	
Gamma/gamma prime-delta (DSE)	Bal.	6	—	—	—	20.0	—	2.5	—	—	
CoTaC (DSE)	—	15.0	Bal.	—	—	—	—	—	—	—	13 $^{v}/o$ TaC

*Nickel-base superalloys normally contain small additions of B or Zr.

To this end, NASA Lewis Research Center developed a nickel-tungsten alloy designated WAZ-20 **(1)** with an incipient melting point of about 1300°C (2375°F). Furthermore, by increasing the amount of gamma prime in the matrix the gamma prime solvus temperature was raised above the incipient melting temperature. In spite of these physical improvements, a stress-rupture life of only a few hours was obtained at 1150°C (2100°F) under a stress of 103 MN/m^2 (15 ksi). It is generally agreed that little opportunity remains to significantly increase the maximum operating temperature of today's best gamma prime strengthened nickel-base alloys by conventional processing methods.

Although cobalt has a higher melting point, 1493°C (2723°F), than nickel, 1454°C (2647°F), cobalt-base alloys are generally weaker than nickel-base alloys below 1100°C (2000°F) and have, therefore, rarely been used for first-stage turbine blades. The strength of cobalt superalloys is obtained from precipitation hardening by carbides and solid solution strengthening. Above 1100°C (2000°F), and for long service times, they tend to retain their strength better than nickel-base superalloys. This high structural stability is evidenced by a relatively flat stress-rupture, time-temperature parameter curve. Thus, cobalt-base alloys have found more application as turbine nozzle guide vanes which generally serve at lower stresses but higher temperatures than turbine blades.

Directional solidification (DS) is a relatively new technique developed largely by Pratt & Whitney Aircraft **(2,3)** for improving turbine blade performance. Individual turbine blades are now being routinely produced with grains running only in the longitudinal direction (Fig. I-5). This is done by pouring metal into a preheated, open-ended investment casting shell attached to a water cooled copper chill. Columnar grain growth is induced in the vertical direction as the blade is slowly withdrawn from the hot zone. This highly oriented structure adds about 30°C (54°F) to the superalloy's temperature capability and greatly enhances ductility (particularly at 700°C) and thermal shock

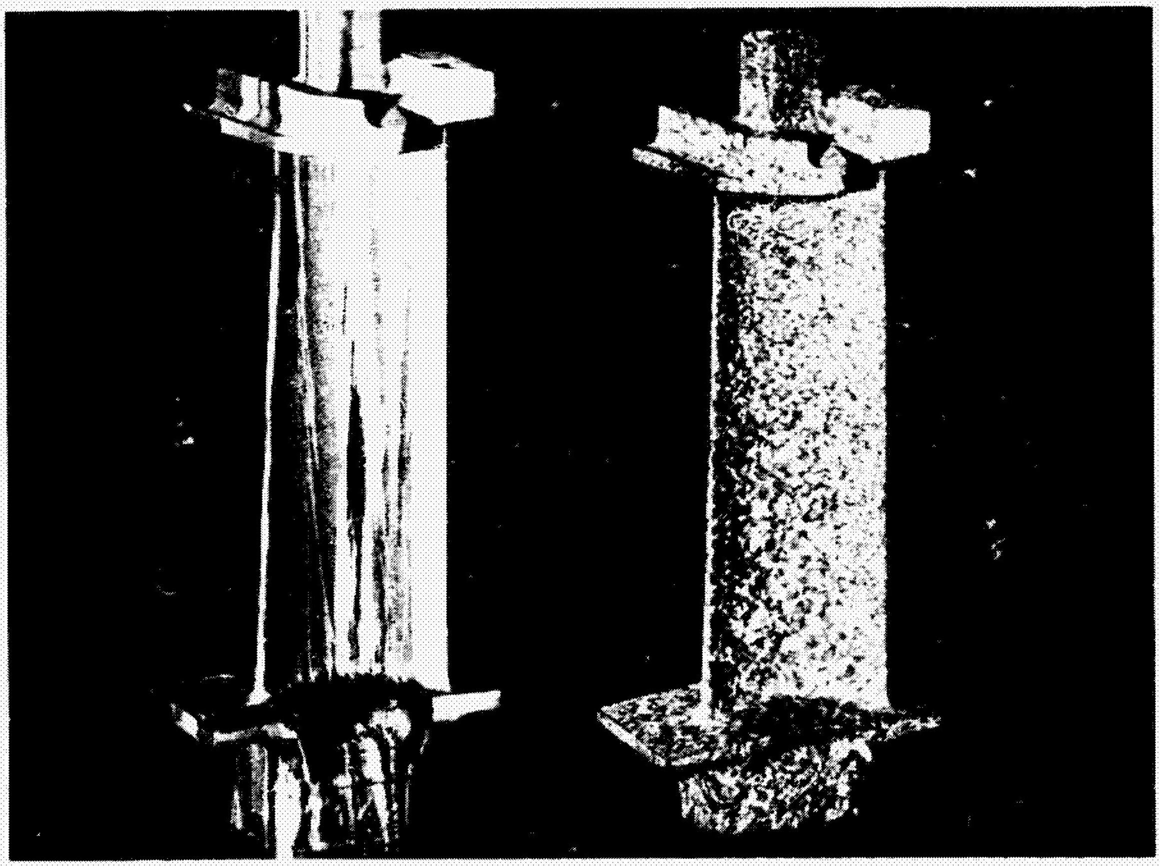

Figure I - 5 Comparison of directionally solidified (left) and equiaxed (right) turbine blades. Photograph courtesy Pratt & Whitney Aircraft and Howmet Turbine Components Corporation.

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resistance. DS castings also offer greatly improved resistance to thermal fatigue which usually manifests itself by cracks initiated at grain boundary intersections with leading or trailing edges of blades. Engine experience with DS airfoils indicates a two-fold increase in life over conventionally cast components under similar stress and temperature conditions **(4)**. As a result, DS airfoils are being used in the latest P & W military and commercial jet engines. Although a DS airfoil can cost up to four times as much as a standard blade, the expense of making the channels required for air-cooling is often eliminated and the net cost of manufacture is reduced.

Directional solidification was first successfully applied to MAR-M 200, a strong but relatively brittle nickel-base superalloy. The stress-rupture properties of DS MAR-M 200, although significantly improved, still fall within the bands of "Best Modern Superalloys" of Figures I-1 and I-2.

Workers at Pratt & Whitney have extended directional solidification to eliminate grain boundaries completely **(5)**. Single crystal nickel-base superalloy castings have been produced that have a lower creep rate and longer rupture life than comparable columnar-grained (DS) material. However, the casting of monocrystal turbine cmponents would be extremely expensive and there are still many technical problems to be solved.

Currently, the maximum temperature capability of wrought superalloys produced by conventional forging or PM techniques is less than that of the best cast superalloys. It is important to note, however, that the Pratt & Whitney Group/Florida has recently been able to obtain significantly improved creep-rupture properties by applying special directional recrystallization (DR) techniques to superalloy material produced by their isothermal superplastic forging (GATORIZING) process **(53)**. For example, DR MAR-M 200 reportedly has about a 30°C (55°F) temperature advantage over DS MAR-M 200.

Of even greater potential significance is Pratt & Whitney Aircraft's new rapid solidification rate (RSR) powder process which is presently being sponsored by the Advanced Projects Agency under ARPA Order 3152 **(5)**. Initial test data indicate that wrought superalloy material can now be produced with elevated temperature properties significantly higher than the best conventional cast superalloys. The RSR process involves rotary atomizing of a molten metal stream and subsequent quenching of the atomized particles in a high velocity stream of helium. Cooling rates in excess of 10^5°C/second have been attained for superalloy powder particles resulting in significant phase supression. Chemical segregation is controlled to a submicron level. The solubility of many alloying elements can be extended without deleterious phase reactions Preliminary testing of wrought material produced from RSR powder and subsequently directionally recrystallized has already indicated that the maximum temperature capability of superalloy turbine blades may be raised by as much as 50-100°C (90-180°F) **(53)**. With new alloy compositions specifically designed to take maximum advantage of the new alloying possibilities presented by the RSR process, it is easy to envisage still farther advances in superalloy temperature capability.

Directionally Solidified Eutectics

The directionality concept is now being applied to superalloy-base eutectic systems with considerable success. By proper alloy selection and unidirectional cooling techniques it is possible to precipitate very strong oriented filaments or platelets of one metallurgical phase in a more ductile matrix of another phase The result is a metal matrix composite created *in situ* during directional solidification (The so called synthesized or artificial composites, such as refractory wire-metal matrix composites, will be discussed in a following section.) The basic process to produce *in-situ* composites is quite similar to that used for DS superalloys except that the airfoil shapes are withdrawn more slowly from the hot zone These *in-situ* composites are considered to be a major innovation in superalloy technology. They offer an attractive new approach toward higher metal operating temperatures.

Figures I-1, I-2 and I-3 present the effect of temperature on the stress-rupture strength of those eutectic alloy systems that have received the most attention and which are most likely to be used in advanced aircraft gas turbine engines. The two basic systems which appear to have the most potential are lamellar eutectics in which the reinforcing phase is delta (δ) or Ni_3Cb, and fibrous (rod-like) eutectics in which the reinforcing phase is an MC carbide, usually TaC SEM photomicrographs of typical rod and lamellar eutectics are shown in Figure I-6 (Ref. **6**). The rupture strengths of two different Ni_3Cb reinforced lamellar composites are shown in Figures I-1 and I-2. The gamma prime-delta ($\gamma'-\delta$) alloy has plates of delta alternating with those of the familiar gamma prime phase of the superalloys. A more recent alloy, gamma/gamma prime-delta ($\gamma/\gamma'-\delta$), has for its matrix phase a nickel solid solution strengthened by a gamma prime precipitate. This alloy has better ductility and oxidation resistance than gamma prime-delta, but has poorer rupture strength at intermediate temperatures and a lower melting temperature **(7 & 8)**.

The most important alloy in the MC fiber eutectic system is CoTaC. A typical microstructure consists of about 13 volume percent TaC fibers in a cobalt alloy matrix containing about 15 weight percent chromium **(9)**. As shown in Figures I-1 and I-2, above 1040°C (1900°F) the strength of CoTaC alloys compares quite favorably with the lamellar composites and the conventional superalloys. Nickel-base MC fiber-strengthened eutectic alloys have also been reported **(9 & 10)**. However, at their present stage of development the NiTaC alloys have rupture strengths only slightly better than conventional superalloys at both intermediate and high temperatures **(6 & 10)**.

Although the most promising eutectic superalloys possess excellent high temperature strength, they tend to have low elongations due in part to the plastic constraint of the matrix by the less ductile reinforcing phase. Work is under way to develop still further advanced or second generation DS eutectic alloys with improved longitudinal and off-axis tensile and creep ductility **(11 & 12)**. Systems receiving the most attention now involve as the prime ingredients Ni, Al, and VI A refractory elements Cr, Mo and W. Ternary monovariant eutectic gamma/gamma prime-alpha (Mo) alloys with improved rupture ductility and processing characteristics have been reported, but the development of eutectics with significantly greater temperature capability appears unlikely. Both nickel-and-cobalt-base eutectics face essentially the same melting point ceiling as conventional superalloys.

At the 138 MN/m² (20 ksi) level, some of the eutectics are up to 100°C (180°F) better than the strongest conventional cast superalloys (Fig. I-2). Most compositions exhibit excellent long [illegible]

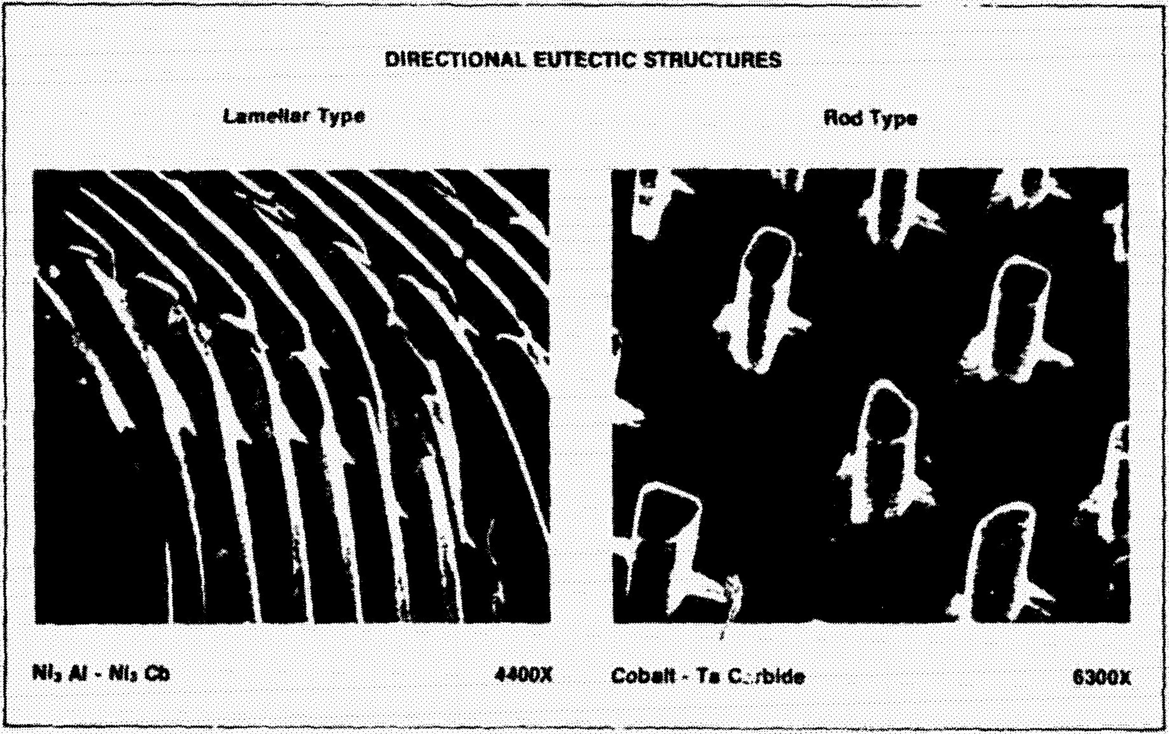


Figure I-6 SEM photomicrographs of etched lamellar and rod eutectics[6].

microstructural stability almost up to their melting points. Their main deficiencies appear to be inherently poor oxidation-corrosion resistance, lack of low temperature ductility, processing limitations and high cost. The slow solidification growth rate common to all systems, typically less than 3 cm/hour, is particularly unattractive when viewed in the context of a low cost integral turbine wheel for a mass produced automotive turbine engine.

Refractory Wire-Superalloy Composites

Refractory wire reinforced superalloys, often referred to as synthesized composites, attempt to combine the high temperature strength of a refractory metal with the oxidation resistance, toughness and ductility of a superalloy. Above 1040°C (1900°F) the best refractory wire superalloy composites have significant strength advantages over the DS eutectics and oxide dispersion strengthened superalloys even when compensated for their high density. The strength properties shown in Figure I-2 for tungsten wire-superalloy composites suggest that they have potential for application to turbine blades and vanes at temperatures to 1200°C (2200°F) and above. The data in Figure I-2 were obtained from specimens containing 70 v/o tungsten wire, without a diffusion barrier, in a nickel-base superalloy matrix **(13)**. Equally good properties have been reported for a 30-45 v/o W-wire composite with a FeCrAlY matrix **(14)**.

In order to allow for the fact that centrifugal loading of a turbine blade is a function of material density, the 1000 hour stress-rupture strength of a 70 v/o W-wire composite (16.3 g/cm^3 density) corrected to the density of a typical highly alloyed conventional monolithic superalloy (8.5 g/cm^3) is shown in Figure I-4. Several DSE alloys, also density corrected, are shown for comparison.

Other refractory metal fibers, such as Cr, Mo and Cb alloys, also have some potential but tend to react with superalloy matrices. To date, none of these alloys have been produced in fiber form with specific strengths equivalent to those of tungsten alloy fibers at temperatures above 1100°C (2000°F).

Possible limitations or barriers to the use of refractory wire superalloy composite materials appear to be: chemical incompatibility between

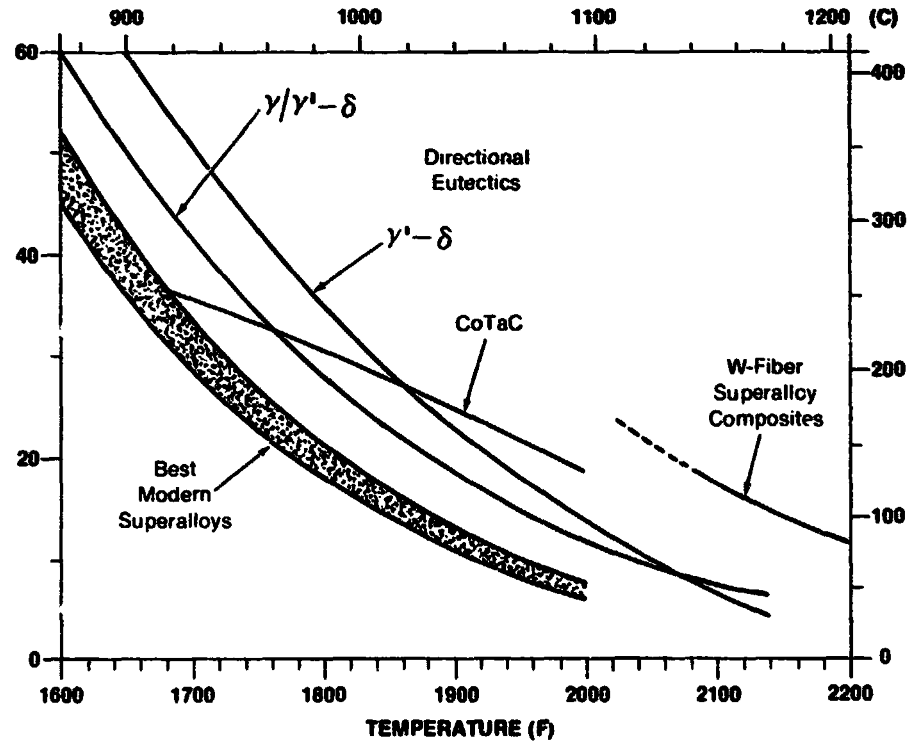


Figure I-4 Density normalized 1000-Hour rupture strengths of superalloys, directional eutectics and W-fiber composites matrix and fiber, high density, oxidation of wires, poor thermal fatigue resistance, limited reinforcement in thin blade walls due to relatively large wire diameter, and cost/complexity of fabricating relatively small turbine wheels. Matrix element diffusion into the wire can cause a significant reduction in wire strength compared to that without matrix-fiber reaction. When suitable barrier coatings are developed, such losses should be reduced or eliminated and further increases in strength and use temperature could be expected. The weight penalty associated with the tungsten wire-superalloy composites can be alleviated to some extent by fiber content variation, or selective reinforcement to reduce average fiber content.

Control of matrix-fiber interaction must be considered during composite fabrication as well as throughout the service lifetime. Thus fabrication processing variables must be selected to minimize the extent of interaction. A great variety of fabrication techniques with wires and fibers have been attempted. They range from the extrusion of a cored billet with fibers preplaced in drilled holes **(15)** to liquid infiltration of a bundle of fibers or casting the matrix around preplaced fibers using investment casting techniques **(16)** Solid state foil-wire compaction **(17)** appears to have the most promise. Table I-2 **(18)** is a summary of actual and potential composite fabrication methods.

Although refractory wire-superalloy composites have demonstrated outstanding high-temperature properties, it is apparent that considerable research remains to be done before they can be considered a viable candidate material for an automotive-size turbine wheel.

Oxide Dispersion Strengthened Alloys

Another class of materials which may allow a substantial increase in operating temperature is the oxide dispersion strengthened (ODS) alloys. The first ODS alloys **(19)**, dispersion strengthened nickel - an alloy of 2-3 v/o thoria in an unalloyed nickel matrix, and later TDNiCr - a similar alloy with improved hot-corrosion resistance, were produced by powder metallurgy techniques. These materials have relatively low strength at intermediate temperatures, but retain their strength effectively at temperatures well above 1000°C (2000°F) because of the presence of fine stable well dispersed oxide particles. For example, TD-nickel in bar form **(20)** has a yield strength of about 69 MN/m^2 (10 ksi) at 1314°C (2400°F) and a 100 hour stress rupture strength at 1200°C (2200°F) of 49 MN/m^2 (7 ksi).

Recently, a new powder manufacturing process known as "mechanical alloying" **(21, 22)** made possible the addition of reactive elements such as aluminum and titanium so that ODS alloys could be further strengthened by gamma prime. Nickel-base superalloys formed by hot consolidation of powders produced by this high energy blending technique have a unique combination of both dispersion strengthening (yttrium oxide) and age hardening (gamma prime) Stress rupture properties of

TABLE I-2
ACTUAL AND POTENTIAL COMPOSITE FABRICATION METHODS

General Method	First Step	Consolidation
1. Power Metallurgy	Pack fibers in matrix or Slip cast matrix about fibers or Use fugitive binder to hold fibers together	Sinter, hot press, or HIP*
2. Foil Metallurgy	Use fugitive binder to bond fibers to foil or press foils about fibers	Diffusion bond in hot press or HIP braze
3. Casting	Cast entire part Cast matrix about fibers	None-when casting entire part. Continuous tapes - hot press or HIP
4. Electro-deposit	Electroplate or form shapes or tapes Electrophoresis	Hot press or HIP
5. Vapor Deposits	CVD, Ion plate, or Vapor-ion beam	Hot press or HIP
6. Metal Spray	Plasma spray or Molten metal spray	Hot press or HIP

*Hot Isostatic Press

commercial alloys of this type such as MA 754 and HDA 8077, are shown in Fig. I-1. These alloys are expected to see service as stator vanes in aircraft turbine engines in the near future.

Several experimental ODS - gamma prime superalloys, WAZ-D **(23)** and MA 755E **(24)**, have recently been reported that have stress rupture properties at 1150°C (2100°F) considerably superior to any known cast superalloy. For example, at this temperature and 102 MPa (15 ksi) ODS WAZ-D has a stress rupture life of approximately 1000 hours. The equivalent turbine blade temperature capability would be about 1040°C (1900°F). See Figure I-2. A special heat treatment, such as zone annealing, appears to be necessary to produce the large elongated grains required for optimum stress rupture properties.

While most of the work on dispersion-strengthening has been expended on nickel-base alloys, a ferritic alloy, MA 956E (FeCrAl + Y_2O_3) has recently been developed **(25)** with stress-rupture properties at 1090°C (2000°F) that slightly exceed those of TD nickel. In addition to excellent oxidation-corrosion resistance, this mechanically alloyed ferritic alloy possesses a high melting point, low density and a low thermal expansion coefficient.

First-Stage Nozzle Guide Vane Alloys

Although first-stage stator vanes are subjected to relatively low stresses they must withstand very high temperatures as the hot gasses entering the turbine section impinge directly upon them. Failure is usually characterized by excessive bowing from gas bending loads, local distortion or cracking from thermal shock, corrosion and/or oxidation, or local melting at hot spots caused by erratic combustion. Both nickel and cobalt-base superalloys have traditionally been used for these static components. Although the carbide-strenghthened cobalt-base alloys have lower strength than the gamma prime nickel-base alloys, up to about 1100°C (2000°F), they are often preferred for their good thermal shock characteristics, weldability, and superior hot corrosion resistance. In addition, the cobalt-base alloys are able to retain their strength more effectively at very high temperatures because the strengthening carbide phase tends to remain in the structure until the alloy is melted. On the other hand, the properties of the strongest nickel-base alloys drop-off sharply when the strengthening gamma prime phase goes into solution and becomes ineffective. This so-called gamma prime solvus temperature is usually somewhat below the incipient melting temperature which can be as low as 1200°C (2200°F) in highly alloyed cast nickel-base superalloys.

The inherent microstructural stability of oxide dispersion strengthened (ODS) alloys gives them a distinct advantage over most of the conventional superalloys for nozzle vanes. The directionally solidified eutectic alloys also have excellent high temperature stability as they are thermodynamically in equilibrium even at their melting point. The DSE's have no significant melting point advantage over cast superalloys, however, as the eutectic phase must melt lower than the matrix.

Because stresses in nozzle vanes are considerably lower then those in blades, maximum vane operating temperature for a given material can generally be greater. Based on typical operating stresses of only about 35-70 MN/m² (5-10 ksi), the approximate 1000 hour vane use-temperatures are as follows: for superalloys 1060° to 1150°C (1950° to 2100°F), for DSE alloys 1120° to 1200°C (2050° to 2200°F); and for ODS alloys 1100° to 1260°C (2000° to 2300°F). Vanes made of tungsten fiber-superalloy composites could theoretically be used up to the melting point of the matrices if the fibers were adequately protected.

Metallurgical Stability

High strength superalloys are susceptible to high temperature oxidation and sulfidation (hot corrosion) in the 650-1180°C (1200°-2150°F) temperature range in which they usually operate. Almost all aircraft gas turbines presently being manufactured require a protective coating on the first stage turbine vanes or nozzles. For the proposed 1370°C (2500°F) TIT engine, the environmental resistance of the blade and vane materials assumes an even greater importance than heretofore. Oxidation must be considered a major barrier to an increased use-temperature for superalloy-base materials

Prolonged exposure of superalloys under stress at temperatures above 1100°C (2000°F) can also result in deleterious microstructural changes that can lead to severe reductions in both strength and oxidation resistance. For this reason, linear extrapolation of stress rupture data to very high temperatures may result in exaggerated lives. In general, alloying requirements for hot corrosion resistance and maximum elevated temperature strength are so different that protection will probably always be required for the strongest superalloys at very high temperatures. For highly stressed turbine blades, the alloy with the best mechanical properties is usually selected, as the superalloy itself cannot be expected to develop a suitable protective scale.

Coatings

It is difficult to develop a coating which is satisfactory over the entire range of temperatures experienced by a blade or vane because some compromise between resistance to hot corrosion and oxidation is usually required. However, when operating temperatures are continuously above about 1000°C (1830°F) very little sulfidation attack takes place, because sodium sulfate becomes unstable, and oxidation resistance becomes the prime consideration.

Essentially all of the important coatings used to protect superalloys have aluminum as the primary constituent. These widely used aluminide coatings are usually applied by pack diffusion, hot dipping, or slurry processes. Regardless of the process, aluminide coatings rely on the inter-diffusion of aluminum, with or without other added elements, and the substrate. In the case of small integral components usually required for a vehicular turbine engine, the diffused coating layer may represent a significant fraction of the blade cross-section and must be considered in stress calculations **(26)**. If the coating thermal treatments are not compatible with the base-alloy treatment, or if the coating is brittle and promotes fracture initiation sites, some further reduction in properties may occur. At very high temperatures the oxidation and diffusion of aluminum are greatly accelerated and the depleted coatings rapidly lose their effectiveness. Cyclic operating conditions tend to induce oxide spalling and cracking exposing the substrate to the environment. Aircraft practice calls for stripping and recoating components with "worn-out" coatings, but this reprocessing would be very expensive and may not be practical on very thin airfoils. Aluminide coatings have been modified to upgrade their temperature capability by the introduction of chromium and by incorporating diffusion barrier layers of tantalum or platinum, but even modified aluminide coatings of acceptable ductility appear to be limited to about 1040°-1100°C (1900° 2000°F).

More recently improved metallic claddings and overlay coatings have been developed. These newer thicker coatings also rely primarily on aluminum oxide or aluminum oxide-rich surface layers to provide oxidation resistance. However, the formation of the coating does not depend on aluminum reaction with the superalloy substrate to form aluminides. The overlay coatings can be applied by electron beam vapor deposition, plasma spray, sprayed slurry or sputtering methods. Hot isostatic pressing is used to produce diffusion-bonded alloy claddings. Most of the coatings are either iron-, cobalt- or nickel-base with aluminum and chromium additions. Some systems also contain one of the rare earths such as yttrium to improve oxide retention during thermal cycling. Cyclic furnace tests and burner rig tests **(27)** have indicated that metallic claddings and overlay coatings may provide superalloys with protection to around 1150°C (2100°F) or about 100°C (180°F) better than the straight aluminide coatings. These newer coating systems are considered very expensive because of the method and difficulty of current production application as well as the relatively high cost of the coating materials. A small integral turbine wheel presents additional coating problems. A 4 to 5 mil build-up on purposely thin trailing edges would probably be unacceptable and the application of a uniform coating to all surfaces of closely spaced integral blades would be extremely difficult because of the line-of-sight restrictions imposed by some of the systems.

In order to take advantage of improved temperature and strength capabilities, directionally solidified eutectics (DSE) also require suitable oxidation resistant coatings. Containing less chromium than many conventional superalloys, most DSE eutectics, as might be expected, exhibit relatively poor oxidation resistance. The standard aluminide diffusion coatings do not provide any significant protection on most eutectic alloys above 1100°C (2000°F) **(28)**. Considerable effort has recently gone into the development and evaluation of suitable overlay coatings for eutectic alloys **(29,30)**

The ODS alloys containing both chromium and aluminum have excellent dynamic oxidation resistance and may be used uncoated at temperatures up to about 1100°-1150°C (2000°-2100°F) **(31, 32)**. Their outstanding oxidation resistance is the result of the formation of a thin very adherent surface layer of Al_2O_3. At higher temperatures and for very long time operation, suitable protective coatings would be required.

Very little data concerning the oxidation resistance of refractory wire reinforced composites at temperatures above 1100°C (2000°F) are available.

Slow moving air oxidation tests around 1100°C (2000°F) indicate that the superalloy matrix can adequately protect tungsten fibers at this temperature although exposed fiber ends will oxidize **(33)**. For higher operating temperatures, the superalloy matrix composition could be designed for maximum oxidation resistance, but some additional oxidation protection would still be required. This protection could be in the form of a conventional superalloy coating or possibly an oxidation resistant bonded outer layer applied during fabrication of the composite **(34)**.

Processing-Turbine Wheels

Investment Casting - Integral Turbine Wheels

An integral turgine wheel would avoid the intolerably high fabrication and assembly costs usually associated with the individual blade-type construction of the aircraft industry. The most practical method for producing a small integral superalloy turbine wheel at this time is investment casting. This process, being historically labor intensive, has yet to supply very many components for high volume automobiles. However, the investment casting process is inherently adaptable to automation and currently great strides are being made towards decreasing labor and material costs while increasing casting quality. Increases in productivity are resulting from technological advances in the use of robots for dipping and stuccoing quick drying shells: automatic wax pattern injection machines, reusable patterns and more efficient metal melting, handling and pouring. Low cost-high volume integral turbine wheels in the future would be produced in entire investment casting plants designed for automation.

A study by Williams Research Corporation in 1973 **(35)** predicted an eventual OEM selling price of less than $10 for a mass produced 2.7 lb. Alloy 713 LC turbine wheel investment casting. Garrett Corporation has developed a modified investment casting process **(36)** specifically for the purpose of mass producing turbine wheels at a lower cost than standard casting techniques. Their AIREFRAC process features a reusable rubber pattern and recycling of some previously expendable foundry materials.

Isothermal Forging-Integral Turbine Wheels

Superplastic forging (GATORIZING) is a potentially low cost process for mass producing integrally-bladed wrought automotive-size turbine wheels that is being investigated by Pratt & Whitney Aircraft Group/Florida under a program sponsored by ERDA **(40,43)**. This process allows forging of complex contoured rotors to close tolerances with very little force. The input weight of expensive superalloy material and machining costs are minimized. The first stage turbine wheel for the Chrysler/ERDA baseline turbine engine served as the demonstration model for the above program. Several integrally bladed wheels were successfully forged with completely filled blades.

The Pratt & Whitney Aircraft Group/Florida has also demonstrated that a directional recrystallization (DR) heat treating process (see previous section on Conventional Superalloys) can be applied to integrally bladed forged turbine wheels **(53)**. Thus by virtue of having blades with coarse elongated grains and a fine equiaxed disc, a DR superalloy wheel should have significantly improved high temperature mechanical properties compared to its conventionally cast counterpart. Still further improvements should be possible through the incorporation of Pratt & Whitney Aircraft's new RSR powder process **(5)**.

Directionally Solidified Airfoil Castings

Efforts are being made to reduce the cost of directionally solidified airfoil castings which, at the present time, are several times more expensive than conventional investment castings For aircraft turbines, the increased service life obtainable with DS blades justifies their extra cost Essentially the same type of equipment is required for the manufacture of both DS superalloys and DS eutectic alloys although the later require much closer control and longer solidification times. The key element in directionally solidifying castings is the attainment and control of high thermal gradiants at the liquid-solid interface

Detroit Diesel Allison Division, under a USAF contract **(37)** has developed a potentially low cost casting process for DS turbine blades that utilizes an exothermic material to economically supply the required high mold preheat temperature and establishes a steep temperature gradiant by extraction of heat through only a chill This process, which may be suitable for automated production, does not require expensive specialized vacuum furnaces equipped with induction coil-susceptor-type mold heating apparatus and furnace cycle times are reportedly significantly reduced.

Also under AFML sponsorship **(38)** Pratt & Whitney Aircraft recently completed a two year program designed to establish a reduced-cost manufacturing investment casting process for producing directionally solidified eutectic airfoil castings For this program, a liquid tin bath cooling process provided the critical heat transfer conditions required for eutectic alloy solidification It was shown that the use of standard investment casting practice, including multiple article molds, commercial crucibles and shell materials and commercial purity alloying elements could produce high quality DSE turbine blades

Investment cast directionally solidified integral turbine wheels have been proposed **(39)** but, because of the extremely close processing controls required, castings of this complexity do not appear to be practical in the time frame of this study

Fabricated Turbine Wheels

Although investment cast integral turbine wheels appear to be expensive by automotive industry standards, any of the alternate methods proposed for fabricating a complete wheel with advanced superalloy material blades would tend to be even more costly. Individual airfoils could be prepared by casting, forging, rolling, or powder metallurgy techniques They could also be machined from rough blanks by electro-machining or by more conventional grinding and milling operations (Machining methods would be unsuitable for most composites if fibers were cut, damaging properties) The bases of the individual blades would probably require additional machining to "fir tree" or some other special shape before being mechanically attached to a machined forged disk Superplastic forging/extrusion of a hub material around the roots of preplaced blades has also been proposed **(40)**. Obviously, the cost of the wheel would increase with increased machining and assembly operations.

Satisfactory joining methods would probably have to be developed before practical turbine wheels or nozzles could be fabricated from directionally solidified castings of advanced composite alloys In this respect, promising results have been reported using conventional brazing techniques and a proprietary diffusion brazing process to join a gamma gamma prime-delta eutectic alloy to Udimet 700 **(41)**. In another study, a gamma/gamma prime-delta alloy was diffusion welded to itself by means of a vacuum hot pressing technique **(42)** A simulated blade-to-base diffusion butt weld was also made between this same eutectic alloy and IN-100

A variety of actual and potential methods for fabricating refractory metal fiber-reinforced composite structures were discussed in a previous section and outlined in Table I-2 The casting methods, which involve preheating the matrix and casting or infiltrating the melt around the fibers, appear to have the most potential for making integral turbine wheels A new mono-layer tape fabrication process employing either alloy foil or powder cloth, has been developed **(17)** that may be applicable to the volume production of individual turbine blades

The thoria (thorium oxide) and yttria (yttrium oxide) dispersion strengthened nickel-base alloys are commercially available only in sheet or bar form Being formable brazeable and somewhat weldable they have found limited use as burner cans and stator vanes Any joining process that melts the base metal tends to cause agglomeration of the dispersoids and must, therefore, be done with caution. Only the newer stronger mechanically alloyed oxide dispersion strengthened materials, such as the experimental ODS + gamma prime alloys, appear to have the potential of being used for turbine blades.

Costs

Fabrication costs can vary drastically depending on the materials and processes used. The cost of a finished turbine wheel could range from 2 to 100 times the cost of the raw materials. An integral wheel construction appears to be the only practical way to avoid intolerably high fabrication costs. The alternative conventional approach of a forged machined disk with inserted blades is not very attractive when considered for a small turbine wheel. However, most of the advanced superalloy materials reviewed in this report can only be produced as individual airfoils or relatively simple shapes at their present state of development. The following section is concerned primarily with the relative costs of producing individual blades out of these materials.

Costs of directionally solidified superalloys are approximately twice those of conventional equiaxed investment castings. The previously referred to study by the Detroit Diesel Allison Division Pilot Foundry **(37)** estimated that a suitable automated production process could eventually produce individual DS blade castings at about a 60 percent increase over equiaxed casting cost. Directionally solidified eutectics should, in turn, cost about twice as much as directionally solidified superalloys **(18)**.

Costs of eutectic blades are likely to remain high because of their low casting rate and the high degree of microstructural perfection required.

The historically high alloy cost of oxide dispersion strengthened materials, about five times that of conventional superalloys, has restricted their use Mechanical alloying, which has recently been scaled-up for large production quantities, should produce significant reductions in the cost of the powders for these materials.

Although the cost of fabricating a tungsten-wire reinforced superalloy airfoil shape would be considerable, the biggest drawback to this composite system is fiber cost. Projected costs **(18)** of the strongest tungsten alloys such as W-Re-Hf-C or W-Hf-C are about $50-$100 per pound for filaments about 0.038-0.064 cm (0.015-0.025 in) in diameter. Casting techniques should be the least expensive of the various fabrication methods. Superalloy matrices produced by metal foil and vapor method or plating and powder techniques would be much higher.

The General Electric MATE Program **(44)** attempted to estimate the potential cost benefits of applying advanced turbine blading to future engines for aircraft predicted for commercial use by 1985. Advanced turbine blading materials analyzed were: W-wire reinforced FeCrAlY, DS eutectics, and ODS + gamma prime alloys. The finished part cost goal for this study was 2½ times the conventionally cast superalloy (René 80) blade cost.

Raw Material Availability And Cost

Rapidly rising prices and politically generated uncertainties in the supplies of key alloying elements, particularly chromium and cobalt, cloud the future for any large scale usage of superalloys in automotive gas turbines Much of our superalloy technology is dependent upon the extensive use of largely imported raw materials. A useful way to look at this potential material utilization problem is to compare the high temperature alloy requirements for the turbine engines that would be produced in a normal car production year with present domestic consumption. This was done in a recent Chrysler study **(45)** utilizing the hot path components of the A-926 Upgraded Engine Table I-3, abstracted from the above study, gives some indication of the impact that a complete transition to turbine powered vehicles would have on domestic metal markets. In addition, a recent study **(48)** by the Jet Propulsion Laboratory (JPL) of the California Institute of Technology made quite detailed estimates of the key elements required for several different advanced automotive turbine engine configurations (both free turbine and single shaft) and related these needs to both U.S and world consumption The possibility of increasing supply and reducing demand of materials, as well as material reserves and their location were also discussed in JPL's report

Most of the metallic elements required in the formulation of superalloys are inherently expensive

TABLE I-3
METALLIC ELEMENT REQUIREMENTS AND COST FOR TEN MILLION AUTOMOTIVE TURBINE ENGINES

	lbs/Engine	Usage Ten Million Engines (Tons)	(46) Percent of 1974 Usage	(46) Domestic Availability (Tons)	Percent of Domestic Availability	(47) Price $/lb	Cost for Ten Million Engines ($1,000,000)
Al	0.287	1800	0.03	630,000	0.296	0.45	$ 1.62
Cb	0.128	640	—	—	—	21.50	27.52
Co	1.11	5550	59.04	0	0	4.90	54.39
Cr	7.26	36300	6.48	0	0	2.44	177.14
Mo	0.29	1450	1.91	76,000	1.91	2.60	7.54
Ni	6.33	31650	15.07	21,000	150.7	2.41	152.55
Ta	0.21	1050	87.5	0	0	42.50	89.25
Ti	0.11	550	2.04	0	0	2.50	2.75
W	0.76	3800	23.3	8,150	46.6	11.00	83.60
							$596.36

The prices of the various elements are also shown in Table I-3. Since about 1970 price increases for almost all of the metals have been very steep. The prices of both electrolytic chromium and cobalt have shown a sharply increasing trend:

Chromium	-	1966, $ .96/lb
		1970, $1.15/lb
		1977, $2.63/lb
Cobalt	-	1972, $2.45/lb
		1974, $3.75/lb
		1976, $5.40/lb

Rhodesia has been the major free world supplier of high grade chromite ore Congressional action now, after repeal of the Byrd Amendment, prohibits the import of Rhodesian chromium alloys and ores There are other major lower grade ore bodies in Turkey and South Africa, but the electrolytic process by which 99.3% pure metallic chromium is made is geared to the higher chromium content of the Rhodesian ore. During the last embargo the Soviet Union, the only other major supplier of high grade chromite, raised prices drastically to take advantage of the shortage. Although chromium is a necessity to both cobalt- and nickel-base superalloys, some savings could result from modifying stainless steel compositions, cladding and other substitutional procedures. On the other hand, high temperature advanced energy generating systems, both those in developing stages and those of longer range interest such as high temperature gas reactors and coal liquefaction systems, will need superalloys **(49)** and large quantities of chromium-containing alloys

About half of the world's deliveries of cobalt and 60% of U.S. consumption come from Zaire **(50)** Canada, the No. 2 producer, supplied only or one-fifth as much cobalt The U.S. is 100% dependent on imports for cobalt, as well as chromium

The supply of nickel, by far the most important superalloy base, is considered to be rather secure with Canada being the principal import source. The price of electrolytic nickel has risen from $1.33/lb in 1971 to a high of $2.41/lb in 1976.

Tungsten has also experienced a steep price increase The price of metallic tungsten powder rose from $3.91/lb in 1969 to $14 51 in June of this year With substantial mining in California, the U S was able to produce slightly more tungsten in 1976 than it imported The high tungsten prices may open lower grade deposits in Canada. Over half of the world reserves of tungsten are located in China

No problem is foreseen in the supply of molybdenum with adequate molybdenite reserves in the U.S. The price of molybdenum has increased more than twofold since 1969.

The major producers of columbium and tantalum, which are often found together, are Brazil and Canada Neither of these two elements have been mined in the U S since 1959. The U S. has extensive reserves of columbium in deposits that are uneconomical to work at current prices

TABLE I-4
STATUS OF SELECTED STOCKPILE MATERIALS

Material (unit)	New Goal	Old "Objective"	In Stockpile	Excess (Shortfall)
Alumina (s.t.)	11,532,000	0	0	(11,532,000)
Aluminum (s.t.)	0	0	5,426	5,426
Bauxite, Jamaica (l.d.t.)	523,000	4,636,000	8,859,000	8,336,000
Chromite, metallurg. (s.d.t.)	2,550,000	444,710	2,46[illegible]55	(65,345)
Ferrochrome, high carbon (s.t.)	236,000	11,476	402,694	166,694
Chromium metal (s.t.)	10,000	0	3,763	(6,237)
Cobalt (lb.)	85,415,000	11,945,000	40,693,000	(44,722,000)
Niobium concentrates (lb.)*	3,131,000	0	1,75[illegible]	(1,[illegible]79,447)
Niobium metal (lb)*	0	36,000		44,851
Maganese ore (s.d.t.)	2,052,000	750,500	3,7[illegible]	1,654,813
Ferromanganese, high carbon (s.t.)	439,000	200,000	60[illegible]	161,000
Manganese metal (s.t.)	15,000	4,750	14,166	(834)
Molybdenum (all forms)	0	0	0	0
Nickel (s.t. Ni + Co)*	204,335	0	0	(204,335)
Rutile (Ti ore) (s.d.t.)	173,928	0	39,186	(134,742)
Tantalum metal (lb.)	1,650,000	45,000	201,133	(1,148,837)
Titanium sponge (s.t.)	131,503	32,329	32,329	(99,174)
Tungsten metal (lb.)	3,290,000	0	1,765,366	(1,524,634)

*Indicates weight of contained metal in alloy or compound.

Abbreviations: lb.-pound; l.d.t.-long dry ton; l.t.-long ton; s.d.t -short dry ton; s.t.-short ton

In a recent report **(51)** prepared for the Defense Advanced Research Projects Agency (ARPA) by the Rand Corporation, the future prospects for materials to be applied in the first stage turbine of man-rated military aircraft were examined. The time horizon chosen was 1990. A method was developed for jointly calculating materials availability and technological risks for alternative gas turbine engine materials. The study concluded that chromium was the only material that posed a significant availability risk to the implementation of high temperature engines for future defense systems. It was recommended that metallurgical grade chromite and/or chromium metal should continue to receive the highest emphasis for U.S. stockpile inventory. Considered of less importance, but still deserving of stockpile consideration was cobalt Although the technology applications of columbium and tungsten were not analyzed, their availability curves suggested that such an analysis might be appropriate.

Stockpiling is one solution for short-term material shortages. For longer range or permanent supply problems, adequate stockpiles could be used to buy the time required for technological substitution. Recent changes in the goals of the U.S. strategic and critical stockpile should be beneficial in this respect **(52)**. Under the new policy there will be separate planning for different tiers of the economy, defense and civilian. Stockpiles can no longer be cut drastically, leaving only enough for an assumed one-year war. The "new goals" and status of selected stockpile materials are given in Table I-4.

The raw material costs for virgin superalloys can be expected to become relatively more expensive over the next five to ten years. Any reductions in the unit costs of superalloy airfoil components for automotive turbine engines would be the result of decreased fabrication costs and lowering of quality standards (as compared to aircraft or military specifications). Automotive specifications should permit recycling of superalloy scrap. This would reduce both alloy cost and mining requirements

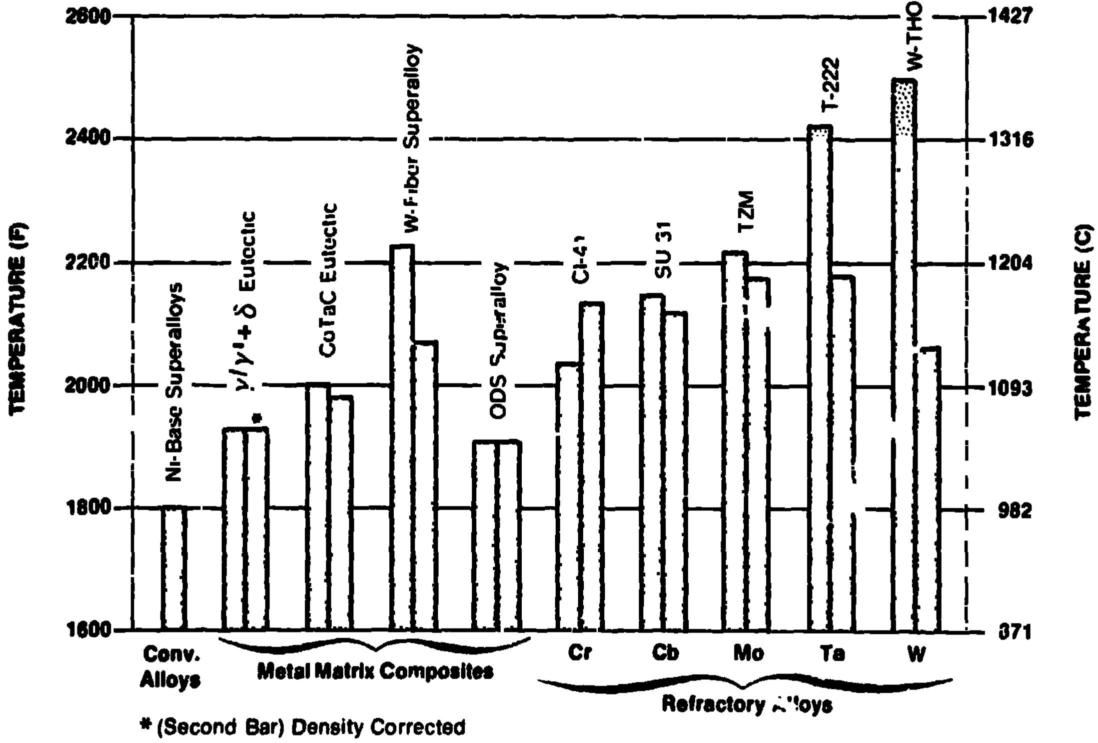
Conventional superalloys, directionally solidified eutectics (DSE), oxide dispersion strengthened alloys (ODS) and tungsten fiber reinforced superalloys were reviewed and compared (Figure I-7) on the basis of "turbine blade temperature capability". For this report, temperature capability was arbitrarily defined as the temperature to produce rupture at 138 MN/m² (20 ksi) in 1000 hours.

Today's best conventional cast superalloys are limited to an uncooled blade temperature of about 980°C (1800°F). Even with continued development and advanced processing techniques, such as directional solidification, this temperature will probably not be extended more than about 25°C (45°F). Wrought superalloys prepared by the usual forging or powder metallurgy techniques do not generally attain the strength of cast alloys in this temperature range.

Significant increases in high temperature properties have been attained by applying the directionality concept to eutectic systems and tungsten fiber superalloy composites. Directionally solidified eutectics offer the possibility of blade temperatures 60-110°C (110-200°F) above those used for conventional cast superalloys. Although tungsten fiber reinforced superalloys afford potentially the highest use temperature capability of any of the superalloy-base systems studied for turbine blades, i.e. about 1200°C (2200°F), their application, because of cost and fabrication problems, is most remote.

Advanced oxide dispersion strengthened alloys with elongated or fibrous grain structures appear to have a potential-use temperature of about 1050°C (1900°F) for blades and up to 1230°C (2250°F) for lower stressed stator vanes. Recently, wrought alloys produced from powder prepared by a new

TEMPERATURE CAPABILITY OF WHEEL ALLOYS
(1000 HR LIFE - 138 MN/m² STRESS-RUPTURE TEST)



* (Second Bar) Density Corrected

Figure I - 7

rapid solidification rate process have been reported that appear to have the potential of increasing the maximum temperature capability of conventional superalloys by about 50-100°C (90-180°F).

With the notable exception of some of the ODS alloys containing both chromium and aluminum, almost all of the advanced superalloy systems mentioned have relatively poor oxidation resistance and will probably require protective coatings at temperature above about 1000°C (1830°F). The standard aluminide diffusion coatings provide long term protection only up to about 1040-1100°C (1900-2000°F). Newer, more costly overlay coatings may extend this range to around 1150°C (2100°F).

Before the advanced superalloy-base materials studied in this report could be considered for a practical small automotive-size turbine wheel, many serious cost, design and fabrication problems would have to be solved. A near net shape integral wheel appears to be necessary to avoid the intolerably high fabrication and assembly costs associated with the individual blade-type construction commonly used for larger aircraft-type turbine wheels. Two processes, investment casting and isothermal superplastic forging, have the potential to produce relatively low cost integrally bladed turbine wheels.

Politically generated uncertainties in the supply of key alloying elements, particularly chromium, and rapidly rising prices cloud the future for any large scale usage of superalloys in automotive gas turbines.

F.A. Hagen
September 30, 1977

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Section II

Refractory Alloys

Section II - Refractory Alloys

Introduction

The high temperature strength requirements imposed on materials by the 1370°C (2500°F) turbine inlet temperature (TIT) automotive turbine engine concept are clearly in excess of the capabilities of conventional Ni-base superalloys. In view of the technical difficulties and high resultant cost of providing air cooling passages in a cast integral turbine wheel there is no possibility of keeping metal temperatures within the usable range of those alloys. Although special processing e.g., directional solidification, tungsten wire reinforcement, etc., does increase their usable strength, the inherent limitation of Ni-base superalloys is their incipient melting temperature which ranges from approximately 1200 to 1315°C (2200 to 2400°F) **(1)**. In recent years high strength ceramic materials possessing ample temperature capabilities and potentially low cost, based mostly on silicon carbide and silicon nitride, have seen considerable advances in the area of properties, fabricability and reliability. Their use in rotating turbine components (i.e. turbine wheels), however, has to date met with only limited success.

The requirements of high melting point, usable high temperature strength, reasonable cost and availability are met, to varying degrees by some members of the refractory metals group **(2)**. They are metals of the three long series in the periodic table. Twelve of them have melting points higher than that of chromium, the commonly accepted lower limit of the refractory group. Rhenium, ruthenium, osmium, rhodium and iridium are of limited availability and their properties need not be considered **(3)**. Hafnium is somewhat more abundant, but little is known of its mechanical properties, its chief use being as an alloying element in superalloys. Vanadium has serious oxidation problems and its melting point is only slightly above that of chromium, offering little advantage over nickel base alloys. This leaves columbium (Cb) and tantalum (Ta) of Group V A, and chromium (Cr), molybdenum (Mo) and tungsten (W) of Group VI A as having melting points significantly in excess of superalloys while occurring in relative abundance in nature

The melting point range of the refractory metals (shown in Figure II-1), from 1875°C (3410°F) for chromium to 3410°C (6170°F) for tungsten, is largely adequate for high TIT engine applications and many of their alloys with suitable high temperature

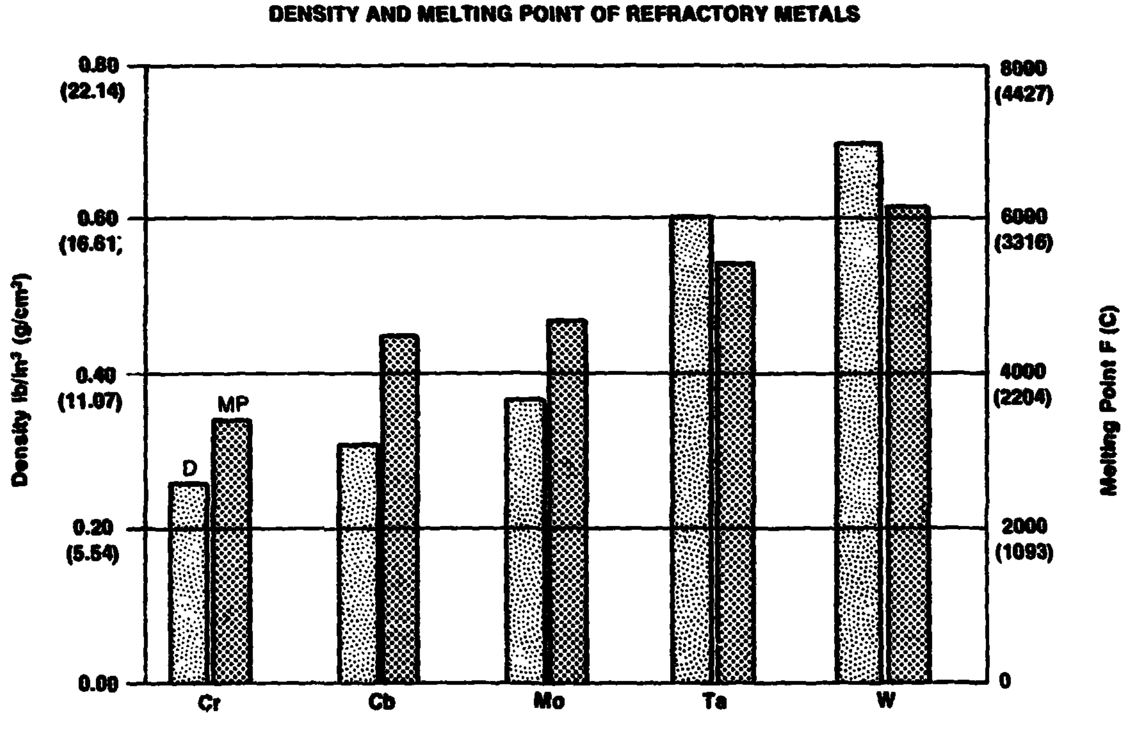

Figure II-1

OXIDATION OF REFRACTORY METALS AT 1000C (2000F)

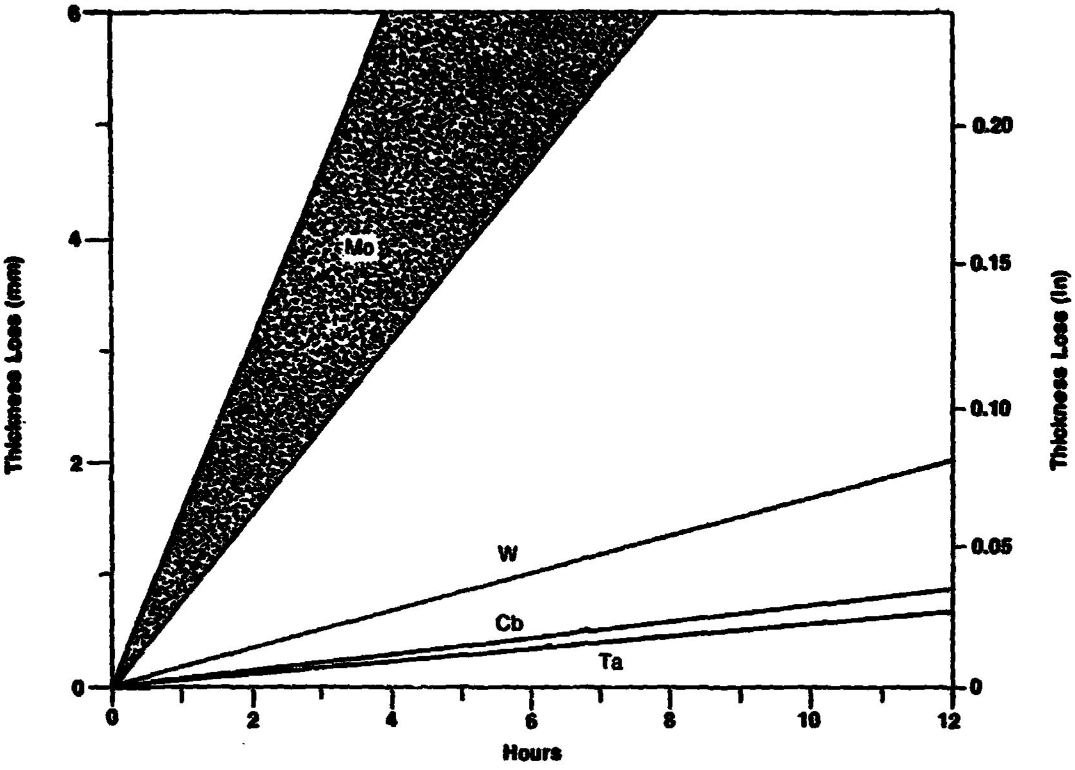

Figure II-2

DBTT OF REFRACTORY METALS

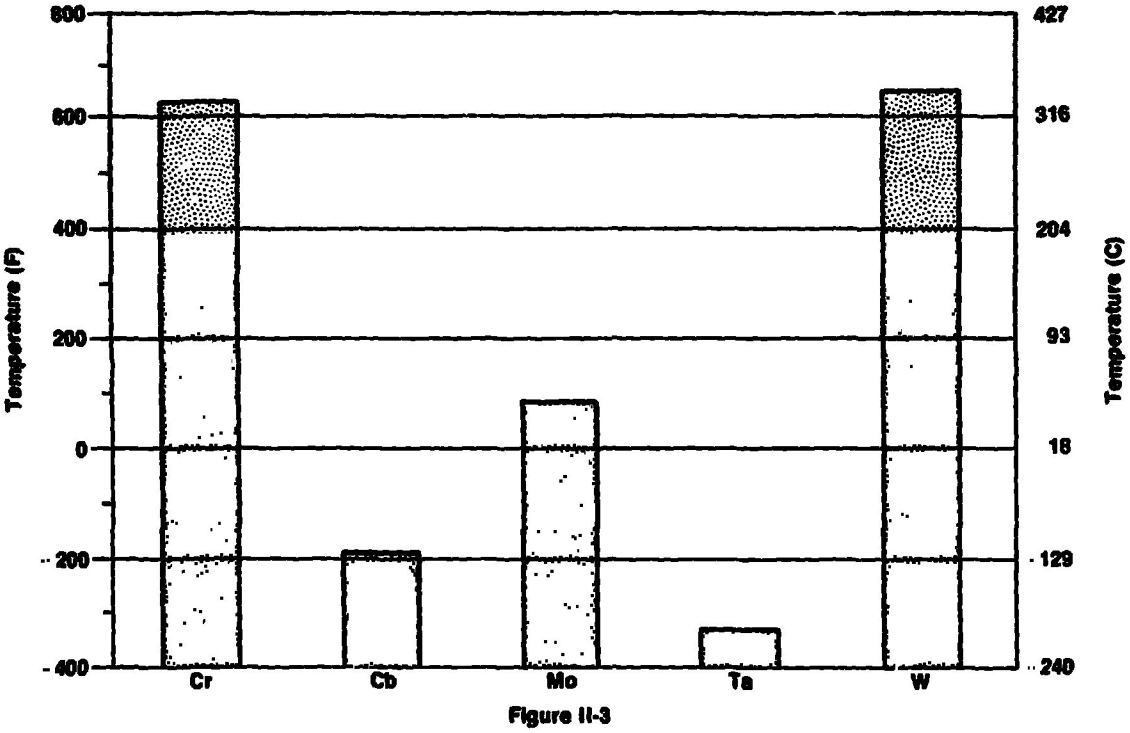

Figure II-3

properties are commercially available. As a group, however, the refractory metals exhibit two serious deficiencies: a poor resistance to oxidation, illustrated in Figure II-2, (or nitriding in the case of chromium) and a high ductile-to-brittle transition temperature (DBTT) characteristic of the metals with the body centered cubic (bcc) structure of Group VI A, i.e. chromium molybdenum and tungsten, as shown in Figure II-3. This latter deficiency has been tempered by proper alloying and processing while the severity of the former is considerably reduced by the use of protective coatings. Of the five refractory metals only chromium has a density lower than nickel; at the other extreme is tungsten with a density of 19.29 g/cm³ (0.697 lb/in³) about twice that of nickel. The use of such high density materials in rotating hardware results in increased centrifugal loading at the blade roots and decreased useful service load carrying strength.

Considerable alloy development work has been expended on the refractory base alloys. Molybdenum alloy research received particular attention in the early fifties when efforts were made to extend the temperature of air breathing engines into a range exceeding the capabilities of the superalloys. Oxidation protection problems were found to be insurmountable and interest waned after an initial surge. Work on chromium alloys was also being carried out since the mid-forties on the basis of their oxidation resistance, their potential cost advantages and as the logical next step in melting point and temperature capability. Serious difficulties were encountered due to their high ductile-to-brittle transition temperature. In the early sixties a new impetus, this time centered on columbium and tantalum, as well as molybdenbum, was given to refractory metals research by the severe materials requirements of rocket engines and space vehicles. However, the majority of those applications involve shorter service lives, higher temperatures and lower stresses than typical turbine engine applications.

Currently all refractory alloys that are available commercially are in the wrought condition and poorly suited to the fabrication of integral turbine wheels of the size contemplated. However, recent research **(31,50,51,54)** has shown that alloys of molybdenum and columbium are amenable to investment casting. Adaptation of the standard investment melting and casting practice to the high melting points and reactivity of the metal has produced usable turbine components.

Chromium-Base Alloys

Several properties make chromium attractive for high temperature applications: a) melting point of 1875°C (3410°F), about 400°C (720°F) above that of Ni and Co; b) good oxidation resistance c) low density, 7.2 g/cm³ (0.26 lb/in³); and d) relatively high modulus of elasticity, 289.6 GPa (42 x 10⁶ psi) **(2)**.

Initial interest in chromium alloys originated at the end of World War II, from their potential usefulness in turbine engines. Their high melting point and oxidation resistance, and their low density offered significant improvements over the existing Ni and Co base alloys in the temperature range of 1000-1200°C (1800-2200°F). The disadvantages of chromium alloys, primarily their high ductile-to-brittle transition temperature (DBTT) of about 300°C (540°F) and accompanying lack of mechanical and thermal shock resistance, and the further embrittlement due to nitrogen pick-up on high temperature atmospheric exposure led to slow initial alloy development. Revived interest followed the development of more ductile yttrium containing and MgO dispersion-strengthened alloys in the late fifties **(4)**.

Strengthening Mechanisms

The addition of substitutional elements is a common approach for increasing the strength of many pure metals. The use of solution strengthening in chromium alloys produces a three- to five-fold improvement over the unalloyed metal. However, those additions also raise the ductile-to-brittle transition temperature to unacceptable levels **(5)**.

Precipitate strengthening is also effective, used singly or in combination with solution strengthening, in improving high temperature tensile properties. Titanium, columbium and tantalum carbides and borides have been found to be effective strengtheners **(6,7)**. Optimum strength is then obtained by solution annealing and aging and has reached a twenty-fold improvement over pure chromium. Stress-rupture properties of a Cr-0.25TaC-0.25TaB alloy (IM-16) are shown in

TABLE II-1
NOMINAL COMPOSITION OF REFRACTORY ALLOYS

Alloys	Cr	Cb	Mo	Ta	W	Hf	Ti	Re	Si	Zr	C	Others
Cr-Base												
C-207	Bal				7.5		0.2			0.8	0.1	0.15Y
Cl-41	Bal		7.1	2.0							0.09	0.1Y
IM-15	Bal			1.7								0.1B, 0.1Y
IM-16	Bal			1.7							0.5	0.5B, 0.08Y
Chrome-30	Bal						0.5					6 MgO
Chrome-90	Bal								0.55			2.5V, 3MgO
Chrome-905	Bal			2.0			0.5		1.0		0.5	2.5V, 3MgO
Alloy-E	Bal			2.0			0.1		0.5			
Alloy-H	Bal			2.0					0.5			0.5 RE
Alloy-J	Bal			2.0					0.5			
Cb-Base												
Cb-1Zr *		Bal								1.0		
FS-85 *		Bal		27.5	11.0					0.9		
C-103 *		Bal				10.0	1.0			0.5		
C-129Y *		Bal			10.0	10.0						0.2Y
FS-291 *		Bal		10.0	10.0							
Cb-752		Bal			10.0					2.5		
SU-31		Bal			17.0	3.5						
WC-3015		Bal			14.5	29.0				1.5		
AS-30		Bal			20.0					1.0		
WD-15		Bal	5.5		9.1	3.9						
VAM-95 (B-99)		Bal			22.0	2.0					0.06	
B-66		Bal	5.0							1.0		5.0V
B-88		Bal			28.0	2.0					0.07	
Mo-Base												
Mo-0.5Ti			Bal				0.5					
TZM *			Bal				0.5			0.08	0.015	
TZC			Bal				1.25			0.3	0.15	
WZM			Bal		25.0					0.1	0.03	
Cb-TZM		1.5	Bal				0.5			0.3	0.03	
Mo-50Re			Bal					50.0				
Mo-30W			Bal		30.0							
Ta-Base												
Ta-10W *				Bal	10.0							
T-111 *				Bal	8.0	2.0						
T-222 *				Bal	9.6	2.4					0.01	
ASTAR-811C				Bal	8.0	1.0		1.0			0.025	
GE-473				Bal	7.0			3.0				
W-Base												
W-1ThO$_2$					Bal							1 ThO$_2$
W-2ThO$_2$					Bal							2 ThO$_2$
W-15Mo			15.0		Bal							
W-50Mo			50.0		Bal							
W-25-Re					Bal			25.0				

*Available commercially

Figure II-4. Ductile-to-brittle transition temperature of those alloys is, however, raised to as high as 482°C (900°F), an unmanageable level. Precipitate strengthening by intermetallic compounds such as $ZrCr_2$ and (ZrCb)Cr has also been used in some alloys, but with limited success **(15)**.

Additions of rhenium have been found to be effective in restoring some ductility ("rhenium ductilizing effect") **(10)** to the brittle alloys, but at an economically impractical level. Other elements such as ruthenium and cobalt have been found to exhibit the same effect **(11, 12)**. Rare-earth additions **(13)** are showing promise in reducing the embrittling nitrogen pick-up on high temperature atmospheric exposure but protective coatings are still thought to be necessary for optimum service life **(14)**.

Ductile alloys strengthened by mechanical dispersion of magnesium oxide have been produced but at the expense of high temperature strength. Thorium oxide dispersions (at the 3 wt% level) produced by chemical vapor deposition (CVD) have also been successful in producing ductile alloys **(16)**. Powder metallurgy techniques are used in their preparation.

Several preferred compositions of developmental alloys have been standardized and are referred to by their originator's designation. Some of the experimental alloys and compositions are shown in Table II-1 **(4,10)**. None of the alloys are available commercially.

Properties

The temperature capability (defined as the temperature at which failure will occur in 1000 hours, at a stress of 138 MPa or 20 KSI) of a high strength chromium alloy, CI-41, is compared, in Figure II-5 with that of nickel-base superalloys and other potential turbine wheel alloys. It can be seen that while chromium alloys offer a significant temperature advantage over the superalloys, the density corrected value adds another 55°C (= 100°F) advantage for rotating components. The stress-rupture properties of some chromium base alloys, compared with Ni-base superalloys in Figure II-4, appear very attractive particularly some of the more recent developments in solution treated and aged tantalum carbide and boride-strengthened alloys. In view of the lower density of chromium (7.19 vs. 8.9 g/cm³ for Ni) these properties are even

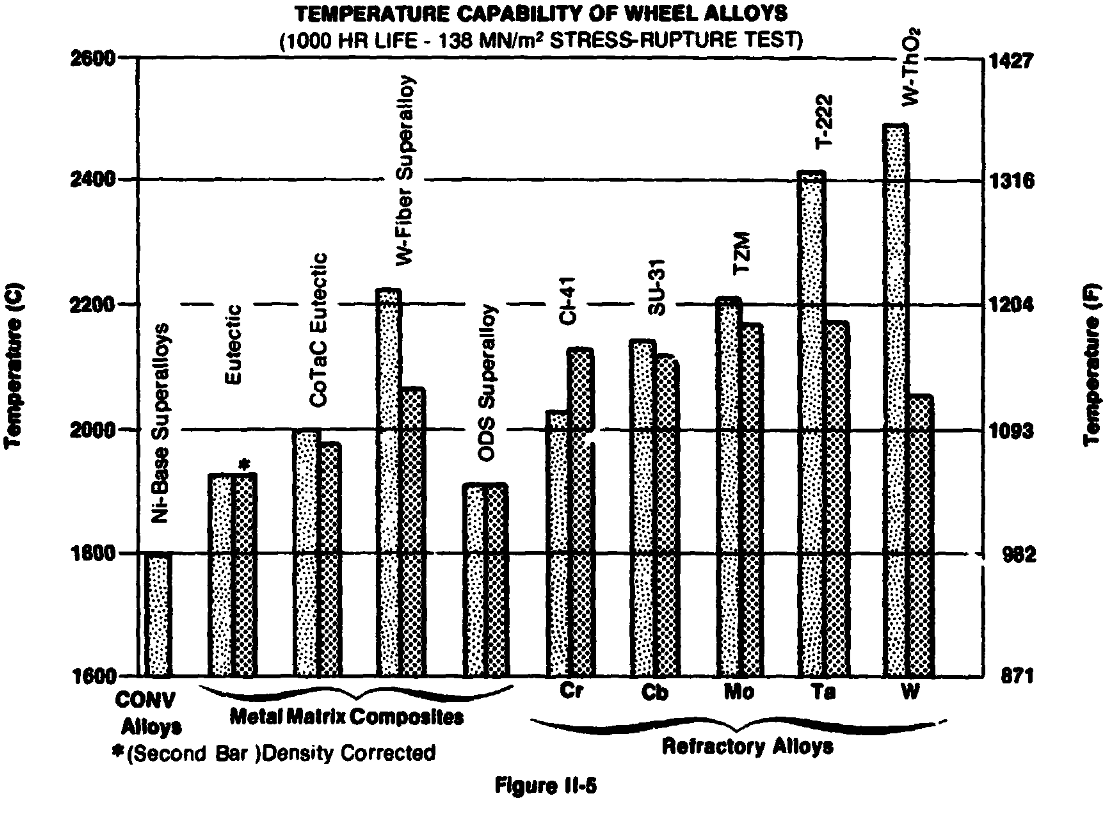

Figure II-5

more attractive for rotating components. The reported DBTT of 260 to 480°C, however, is unacceptably high.

Fabrication

Early research work on chromium alloys used electrolytic chromium flake until it was realized that a high interstitials content, particularly nitrogen was responsible for some of the low ductility and the difficulties in interpretation of the results. The development of iodide chromium, in the early fifties, and later of purification techniques for electrolytic chromium spurred the researchers and resulted in a better understanding of the chromium based systems and some measure of control of the DBTT problems **(5)**. Ingots of pure and alloyed chromium can be produced by arc-melting, skull melting, induction melting or by the powder route. Primary breakdown is normally by extrusion or press forging for the more ductile alloys.

No successful investment casting of integral wheels or shapes has been reported.

Coatings

The sensitivity of chromium and chromium alloys to embrittlement by nitrogen upon exposure to air at temperatures above about 1100°C (2000°F) precludes their use without protection in the form of coatings impervious to nitrogen diffusion. Various coating systems based on silicides, aluminides and borides **(17)** or containing yttrium, lanthanum and hafnium **(14)** have been explored with varying degrees of success. The life of experimental Fe-modified silicide coated chromium alloy samples has exceeded 100 hours, while yttrium and chromium-yttrium-lanthanum coatings have shown simulated service lives of over 200 hours at 1150°C (2100°F).

Nickel alloy claddings have also been investigated **(18)**, with service lives of up to 600 hours at 1100°C, but with a loss of bend ductility due to interdiffusion between cladding and sample. The requirement of integrity of the coating after repeated thermal cycling is essential but difficult to attain.

100 HR S-R STRENGTH OF CHROMIUM ALLOYS

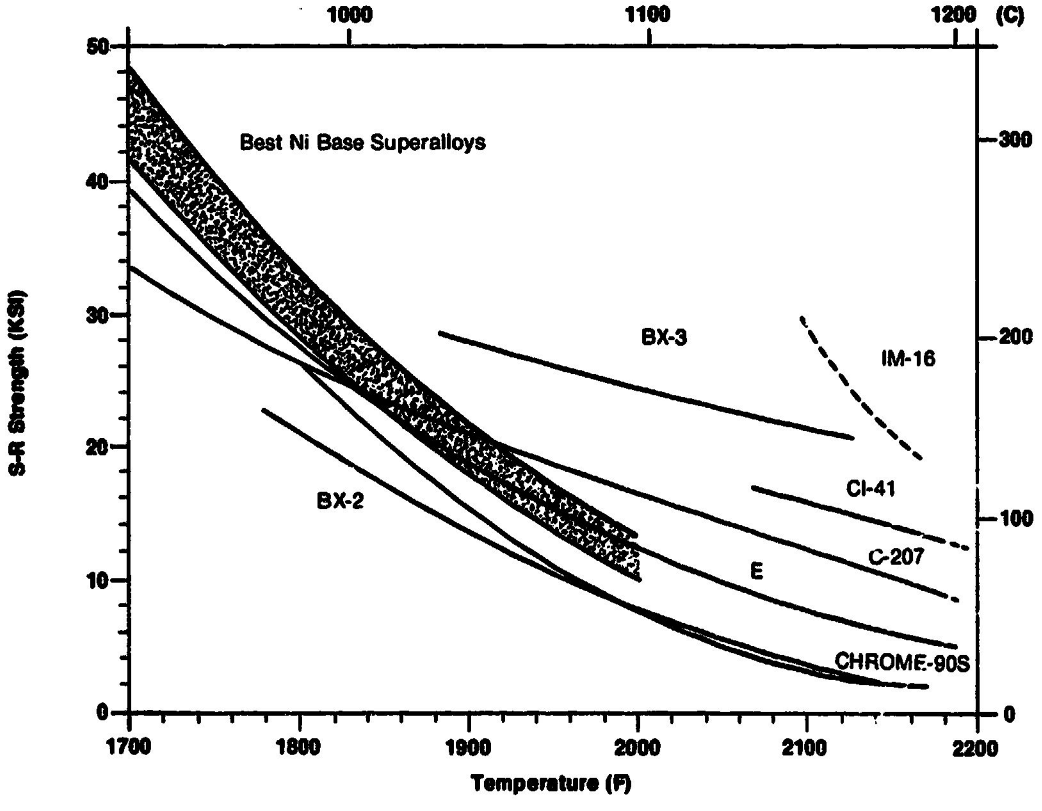

Figure II-4

Columbium (Niobium)-Base Alloys

In common with other refractory metals, columbium has a high melting point, 2470°C (4475°F), that makes it attractive for high temperature applications In addition, its density of 8.57 g/cm^3 (0.31 lb in^3) is about equal to that of nickel (and nickel base alloys) and much less than that of molybdenum, tantalum or tungsten (see Figure II-1) It also has good ductility at low temperature, and although it is oxidation prone, the major oxide is stable up to 1500°C (2550°F) **(2)**.

The early work on columbium dates back to the mid-fifties and early sixties when the desirable high temperature properties of the metal were recognized. Since then the technology of columbium and its alloys, under the impetus of the space and nuclear energy programs, and the continuing development toward higher TIT turbine engines, has progressed to the stage of commercially available alloys. Several reviewers **(1,3,37)** have pointed out tnat the properties of columbium make it an outstanding candidate for high temperature turbine applications. Its low ductile-brittle transition temperature, the refractoriness of its oxides and the high melting point, which promises high strength at service temperature, are particularly attractive to engine developers The DBTT of the pure metal, −120°C (−185°F) is raised by alloying but in general it remains below room temperature **(1,20)**. Protective coatings also raise the DBTT of some alloys, the bend ductility of WC3015, for instance, is lowered by silicide coatings **(21)**

Strengthening Mechanisms

Addition of various solute elements to columbium results in increased hardness and strength **(2)** through the common phenomenon of solid solution hardening. The degree of strengthening depends on the solute element and the amount added and can be correlated with a change in lattice parameter. This suggests that atomic size misfit plays a dominant role in the process **(22)** At low solute concentration a certain degree of softening occurs, but unlike that occurring in Group VI metals (Cr, Mo, W), it is ascribed to the scavenging action of the solute on embrittling interstitials Hafnium, tantalum and tungsten are the commonly used solid solution strengtheners in columbium alloys. Because of the relatively high concentration of those high density elements required for useful strength the low density advantage of columbium is partially nullified The density of the stronger alloys can be as much as 25% greater than nickel alloys resulting in an appreciable weight penalty **(1)**.

Although the DBTT of the pure metal is low, alloying at the required high level can severely decrease the ductility of the material, and its fabricability.

Precipitation strengthening, by hafnium and zirconium carbides, is also used with some success, usually in addition to solution strengthening.

Interstitial alloying elements such as oxygen and nitrogen also strengthen columbium and columbium alloys **(20,23)**. An oxygen level of less than 1000 ppm in a Cb-1Zr alloy produces an appreciable increase in strength **(24)** Increasing strength occurs with increasing oxygen content to approximately 6000 ppm, with accompanying decrease in ductility Severe embrittlement, at room temperature, is also known to occur by hydrogen absorption at relatively low levels **(25,26)** Carbon contamination such as from oil vapor during vacuum creep testing, has been found to produce excessive brittleness in a Cb-25Zr alloy **(27)** The detrimental effects of minute amounts of gaseous interstitials particularly renders the use of protective coatings imperative

In some of the complex alloys, variations in thermo-mechanical treatment are used to optimize selected properties annealing of the wrought material for optimum stress-rupture strength or solution treating and aging for best creep properties **(19,87)**

A number of columbium alloys have been fully characterized and given a commercial designation The bulk of their applications is in the aerospace and nuclear fields They are shown in Table II-1

Properties

Temperature capability of a well-established commercial alloy (SU-31) is seen in Figure II-5 to offer a strength advantage of approximately 195°C (350°F) over conventional Ni-base alloys Stress-to-rupture properties of selected columbium alloys are shown in Figure II-6, also compared to conventional Ni-base superalloys Their rupture strength is found to increase in rough proportion to the amount of contained strengthening elements with an accompanying increase in density This strength advantage, claimed to be marginal in commercial turbine engines where air cooled superalloy blades can be used, is real in an automotive turbine where size precludes such artificial means of keeping metal temperature at a manageable level. A serious limitation of all the columbium alloys, however, appears to be a relatively high creep rate which results in undesirable permanent stretching in service **(28)**. Some typical values are shown in Table II-2. Another limitation of columbium alloys is a low yield strength in the intermediate temperature range (400 to 800°C) which could affect turbine blade root design **(1,34)**.

High rupture strength and lower creep rates can be obtained in some of the precipitation strengthened alloys, such as AS-30 and VAM-97, by the proper combination of thermal and mechanical treatments **(19,29)**. Typical rupture strength values are shown in Figure II-6. The effectiveness of the treatments varies according to the alloy but their use is limited by the final physical size and complexity of the part. Limited data is available on the cast columbium alloys but stress rupture properties of cast alloy C-103, (Cb-10Hf-1Ti) are reported comparable to that of the annealed wrought material **(30)**.

Some alloys, such as WC-3015, are claimed to have improved oxidation resistance due to their high hafnium content **(31,32)**, but it is doubtful that the protective oxides formed can withstand the severe conditions of thermal cycling, gas impingement and erosion encountered in the 1370°C TIT engine without any additional protection **(19,29)**.

Fabrication

Consolidation and alloying of columbium, from high purity powder, are commonly done by electron beam melting to keep interstitial impurities at a low level. Homogeneous alloy ingots are obtained by consumable-electrode arc melting. Ingot breakdown is usually by press forging or extrusion above 870°C (1600°F). In the case of the higher strength alloys breakdown is by extrusion at temperatures up to

100 HR S-R STRENGTH OF COLUMBIUM ALLOYS

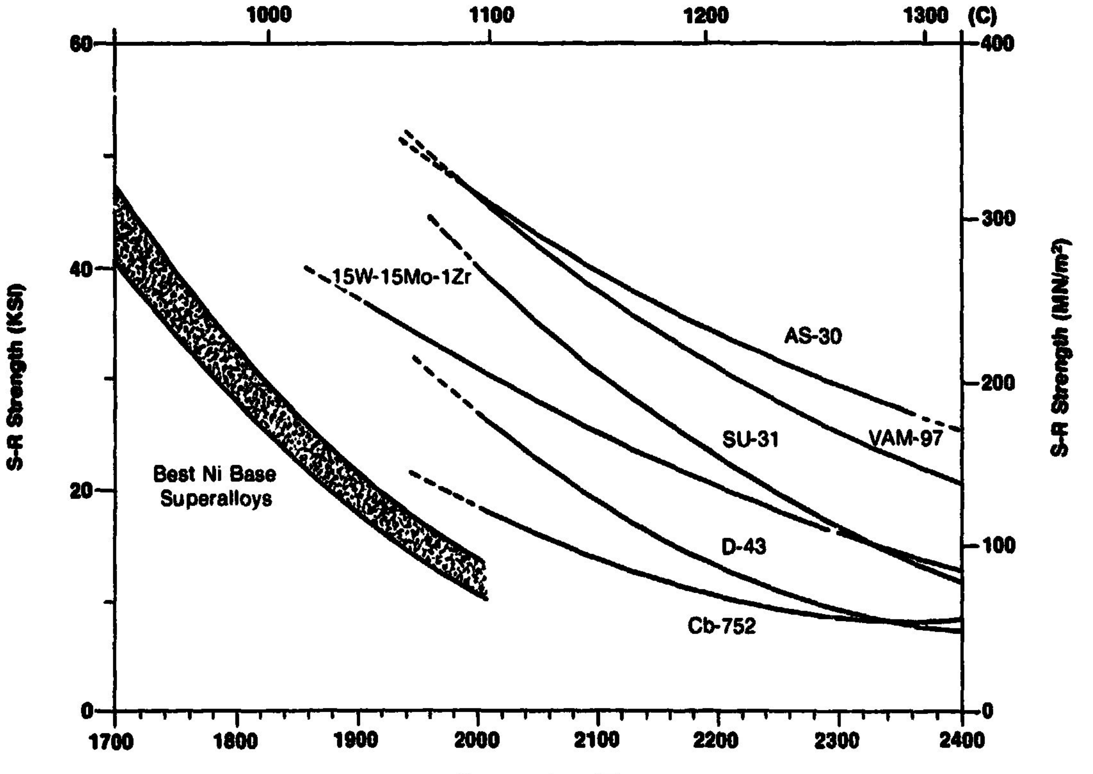

Figure II-6

1650°C (3000°F). Following surface conditioning and recrystallization (annealing) the ingots are reduced to a variety of mill products by mechanical working at the proper temperature.

A relatively recent development is the successful investment casting of four standard alloys previously used only in the wrought condition: SU-31, Cb-752, C-103 and C-129Y **(33)**.

Coatings

Although some of the commercial and developmental columbium alloys possess improved oxidation resistance, compared to the pure metal, protective coatings are required to obtain adequate service life at the temperatures envisioned in the new engine. Of the many coating systems that have been investigated for columbium alloys only the silicides have given acceptable long time protection. However, they are somewhat lacking in ductility and are marginal in impact resistance. They are based on silicides of Cr, Ti, Fe, Mo, W and V and are applied by pack cementation or fused slurry techniques **(34,37)**. Modification of the thermal expansion of the coatings to better match that of the substrate by incorporation of dispersed discrete particles has been proposed to compensate for the low ductility **(36)**.

Sylvania's R512A (Si-20Cr-5Ti) and R512E (Si-20Cr-20Fe) are commonly used coatings of the fused slurry type **(35,39)**. However, investment cast SU-31 (Cb-17W-3.5Hf-0.1C) vanes coated with R512E and tested under simulated engine conditions **(39)** were found to have poor cyclic oxidation and thermal fatigue properties.

A recent development in coatings for columbium alloys is Solar NS-4 **(37,38)**. It is a two cycle coating in which the part is first sprayed with a tungsten alloy modifier (W-20Mo-15Ti-15V) and vacuum sintered, followed by pack siliciding. Coated parts have withstood 1000 hours of oxidation testing at 1316°C (2400°F) and 520 hours at 1370°C (2500°F) and 500 thermal cycles between 260°C (500°F) and 1370°C (2500°F) in an oxidation/erosion rig without failure. External radii as small as 0.25mm (0.010") were successfully protected. Some difficulties were experienced in protecting internal surfaces such as air cooling passages.

TABLE II-2
CREEP OF COLUMBIUM AND MOLYBDENUM ALLOYS

Time for 1% Creep at 138 MPa and Indicated Temperature

Alloy	Condition	Time for 1% Creep			Larson-Miller	Reference
		1090°C (2000°F) hrs	1200°C (2200°F) hrs	1315°C (2400°F) hrs	Parameter $T°R(20+\log t)\times 10^{-3}$	
Columbium Alloys						
SU-31	Wrought	2897	50		57.71	84
D-43	t-m-t**	60	3		55.2	85
FS-85	Wrought	10	0.4		51.65	86
VAM-97	t-m-t	110,500	1447	35	61.6	27
AS-30	Wrought	9	0.4		51.5*	87
Molybdenum Alloys						
TZM	t-m-t	14230	217		59.41	47
TZM	Wrought	5957	97		58.48	87
TZM	Recrystallized	7320	117		58.7	47
TZM	Cast		8171	173	63.6*	54
Mo-Hf-C	t-m-t		50000	942	65.7*	46
Mo-Re-Hf-C	t-m-t		35600	683	65.3*	44

*Extrapolated
**thermo-mechanically treated

Molybdenum-Base Alloys

The attractive properties of molybdenum for high temperature applications are a high melting point. 2620°C (4730°F); a relatively low density, 10.22 g/cm^3 (0.369 lb/in^3); a high modulus of elasticity, 317 GPa (46 x 10^6 psi); and an excellent strength-to-weight ratio at high temperature **(2)**.

Molybdenum was the first refractory metal available in sufficient quantity to be considered for high temperature structural applications. Prior to 1939 volume usage of the pure metal was restricted to incandescent lamp and vacuum tube manufacturing **(40)**. After World War II the pure metal became available in larger tonnage and its high temperature properties better documented. During the nineteen fifties jet engine manufacturers were planning to increase the TIT by several hundred degrees and were looking toward refractory alloys for suitable materials. The first attempts to take advantage of the high temperature tensile and creep properties of molybdenum occurred during that period **(41)** when General Electric ran a turbine wheel with forged molybdenum alloy blades for 250 hours at 1230°C (2250°F). The blades were fabricated from Mo-0.5Ti, the only commercial alloy then available. Various oxidation resistant coatings were used to protect the blades, but oxidation failure still was the life-limiting factor in the engine tests. In the late nineteen fifties TZM (Mo-0.5Ti-0.08Zr0.025C), an alloy with improved properties, was developed **(42)** with significant advantages over molybdenum metal with respect to high temperature strength and resistance to recrystallization. The alloy, which has been available commercially since the early sixties, was originally developed for aerospace use but has since found a wide range of commercial applications particularly in the die casting industry.

Strengthening Mechanisms

All three conventional strengthening mechanisms; solid solution, precipitation and strain hardening, are effective in strengthening molybdenum and its alloys. While small additions of certain elements such as aluminum, chromium, silicon, iron, cobalt and nickel produce an initial softening **(43)**, most elements, specially those of Group IV A (Zr, Hf, Ti), promote strengthening at relatively low levels of alloying **(44)**. However, fabricability decreases rapidly with increasing solute content and the already high DBTT of the pure metal can be raised to impractical values.

Solid solution strengthening was emphasized in the early development of molybdenum alloys. Small additions of titanium (up to 0.5%) were found to increase the strength, raise the recrystallization temperature and improve the marginal ductility of the unalloyed metal, forming the basis for the commercially important Mo-0.5 Ti alloy, the only refractory alloy available in 1955. The alloying addition was then thought to provide solution hardening. However, carbon control, at a critical C/Ti ratio, was found to be the key to optimum strength in titanium containing alloys; dispersion strengthening by precipitated titanium carbide being the hardening mechanism. Further additions of zirconium and improved carbon control resulted in further strength improvement.

Two levels of additions were eventually adopted: 0.5Ti-0.8Zr-0.015C and 1.25Ti-0.3Zr-0.15C; they constitute the well known alloys TZM and TZC. The higher level of alloying elements produces higher strength but also results in marginal low temperature ductility and fabricability.

The effectiveness of precipitated Group IV A carbides in increasing the strength of molybdenum-base alloys is somewhat proportional to their thermodynamic stability **(10,45,46)**. Recent studies have shown that hafnium carbide is a more potent strengthener than titanium and zirconium carbides; improved ductility also results from the hafnium additions **(47)**. The carbide strengthened alloys are amenable to solution-annealing and aging treatments.

Significant further improvements in strength of the carbide dispersion strengthened alloys are also produced by strain hardening **(43,48)** (working below recrystallization temperature) during primary or secondary fabrication. The mechanism of strain hardening is related to the mutual interaction of dislocations and the barriers to their movement within the lattice. Dislocation density increases with increasing deformation resulting in a higher state of internal stress. In body-centered-cubic metals (including the refractory metals) the formation of jogs at the intersection of screw dislocations is thought to be the principal mechanism. Experimental studies have confirmed the mechanism and its effectiveness in carbide dispersion strengthened alloys **(49,50)**. These strain hardening effects can produce increases up to 20%

over the strength of the annealed metal and its alloys, and are retained to high service temperatures, close to recrystallization. The recrystallization temperature of pure molybdenum, 1177°C (2150°F) is raised considerably by alloying even at the low levels of additions of the commercial alloys. Thus the recrystallization temperature of Mo-0.5Ti is raised to 1343°C (2450°F), TZM to 1427°C (2600°F) and TZC to 1536°C (2800°F). This increase allows retention of the strain hardening effects to high levels of service temperatures. Thermo-mechanical processing combines structural strengthening and strain hardening in varying sequences for properties optimization. Its use, however, is limited by the shape of the finished product.

Rhenium additions have been found effective, as in chromium alloys, in lowering the DBTT ("rhenium ductilizing effect") of molybdenum alloys. Alloys containing 25 to 35% Re have considerably improved fabricability and ductility.

A new series of experimental alloys, based on the system molybdenum-nickel has shown some promise, particularly in regard to oxidation resistance and castability. However, serious high temperature strength and stability problems remain to be solved **(51,52,53,54)**.

The commonly available molybdenum alloys, their compositions and their commercial designations are shown in Table II-1.

Properties

Pure molybdenum was the first refractory metal used for its hot strength. Even unalloyed the high temperature tensile strength, stress-rupture strength and useful temperature range of molybdenum exceeded those of the superalloys then available. Those high temperature properties have since been surpassed by alloys of molybdenum and additional gains have been obtained by optimizing their thermomechanical treatments. The temperature

100 HR S-R STRENGTH OF MOLYBDENUM ALLOYS

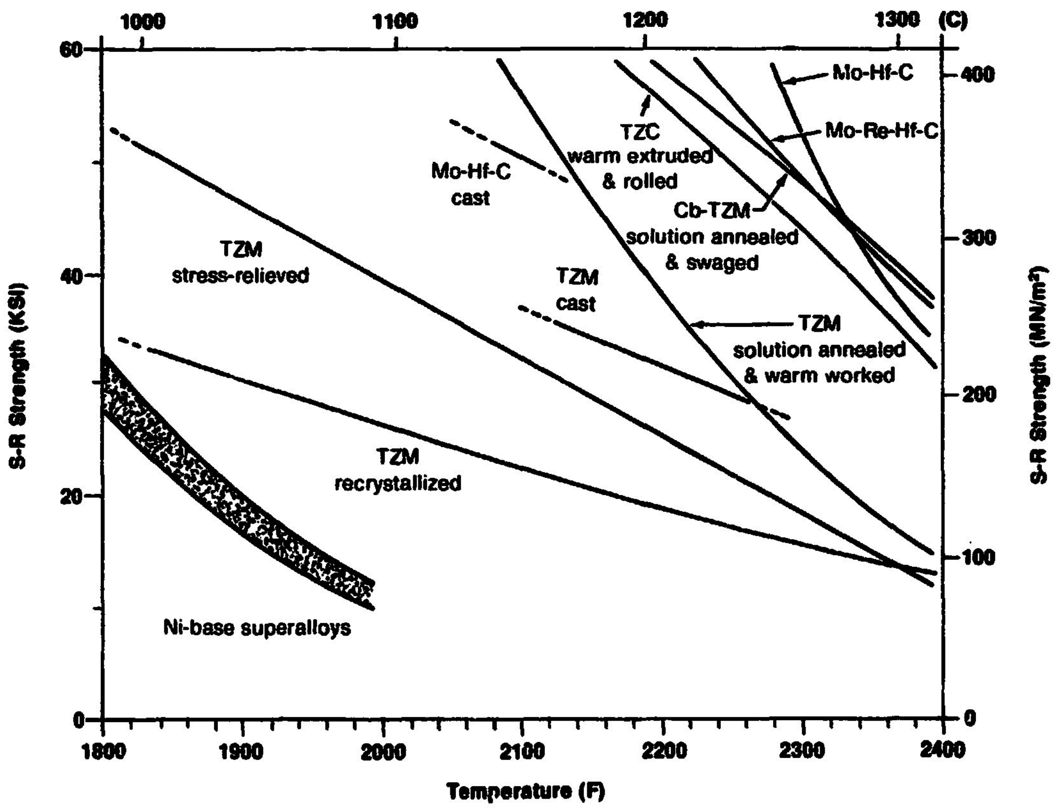

Figure II - 7

TABLE II-3
TENSILE PROPERTIES OF CAST AND WROUGHT TZM

	Cast TZM			Forged TZM (Stress-Relieved)		
Temperature	**U.T.S.**	**Y.S.**	**El.**	**U.T.S.**	**Y.S.**	**El.**
°C (°F)	MPa (ksi)	MPa (ksi)	%	MPa (ksi)	MPa (ksi)	%
23 (73)	293.7 (42.6)	246.8 (35.8)	1.5	907.9 (131.7)	822.5 (119.3)	23.7
815 (1500)	270.2 (39.2)	—	29.4	646 (93.7)	620.5 (90.0)	13.3
1095 (2000)	244 (35.4)	179.9 (26.1)	22.1	552.9 (80.2)	521.2 (75.6)	15.1
1205 (2200)	255.1 (37.0)	—	19.9	401.2 (58.2)	—	22.9
	(Ref. 54)			(Ref. 55)		

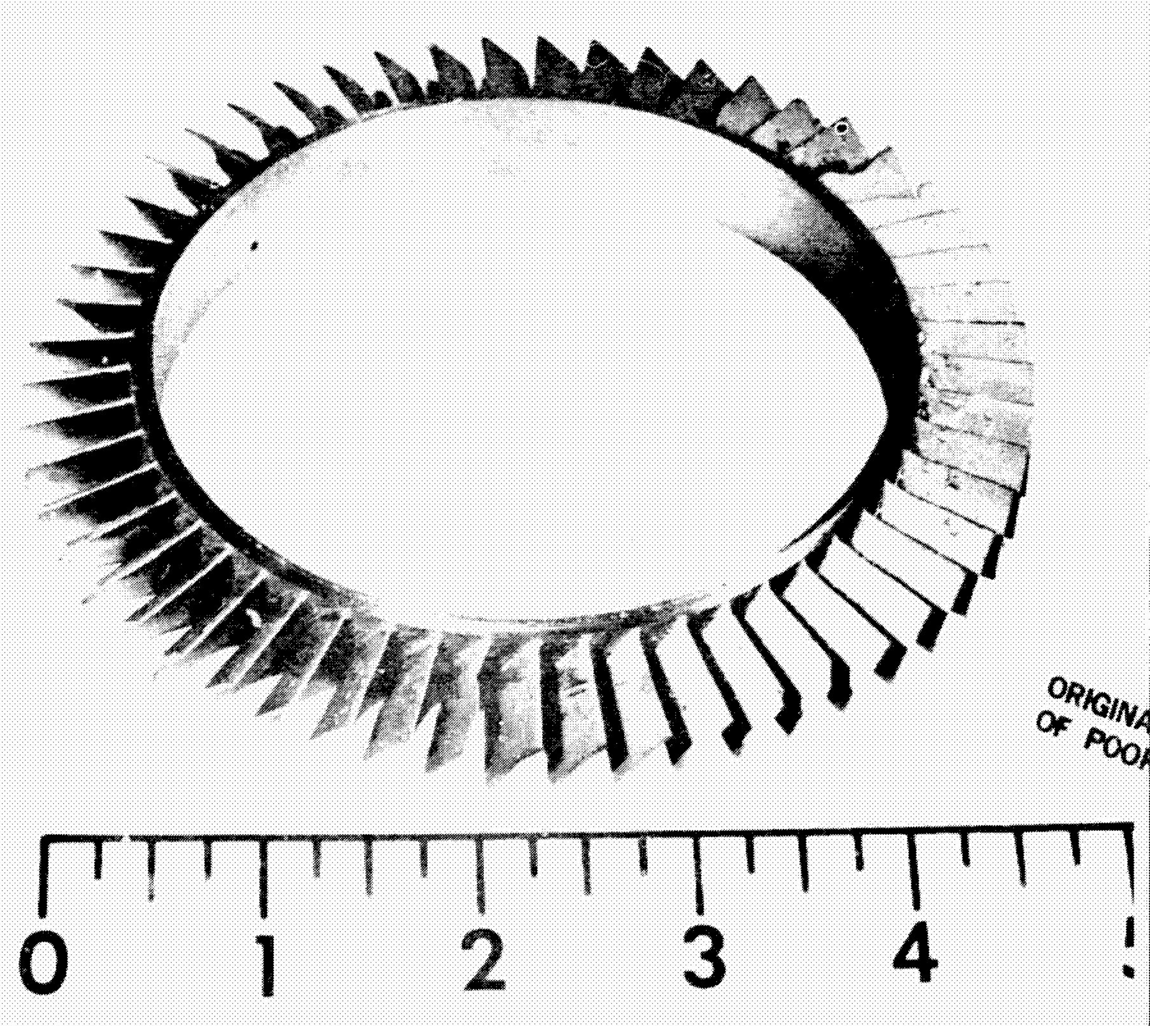

Figure II-8 Investment cast TZM blade ring. (Photo courtesy of Climax Molybdenum Co. of Michigan.)

capability of TZM, the best known commercially available alloy of molybdenum (in the wrought and stress-relieved condition) is shown in Figure II-5 compared with other potential high temperature engine materials and conventional nickel-base superalloys. Stress rupture strengths (100 hr.) of various commercial and experimental molybdenum alloys are depicted in Figure II-7. The wide range of useful properties is shown to extend to temperatures as high as 1315°C (2400°F). The highest strengths are reported for thermo-mechanically treated modifications of the standard TZM and dispersion strengthened hafnium carbide-containing alloys **(40,44,46,47)**. Heat treatment and service below the recrystallization temperature retain all or a major portion of the strain hardening, an important contributor to the strength of the alloys. Also shown are the properties of investment cast standard TZM alloy; they are reported for bars machined from a simulated turbine wheel disk and appear adequate for the normally expected blade stresses **(56)**.

Short-time high temperature tensile properties of cast **(56)** and wrought **(57)** TZM are shown in Table II-3. The yield strength of the cast alloy, an important design criterion for the compressor wheel

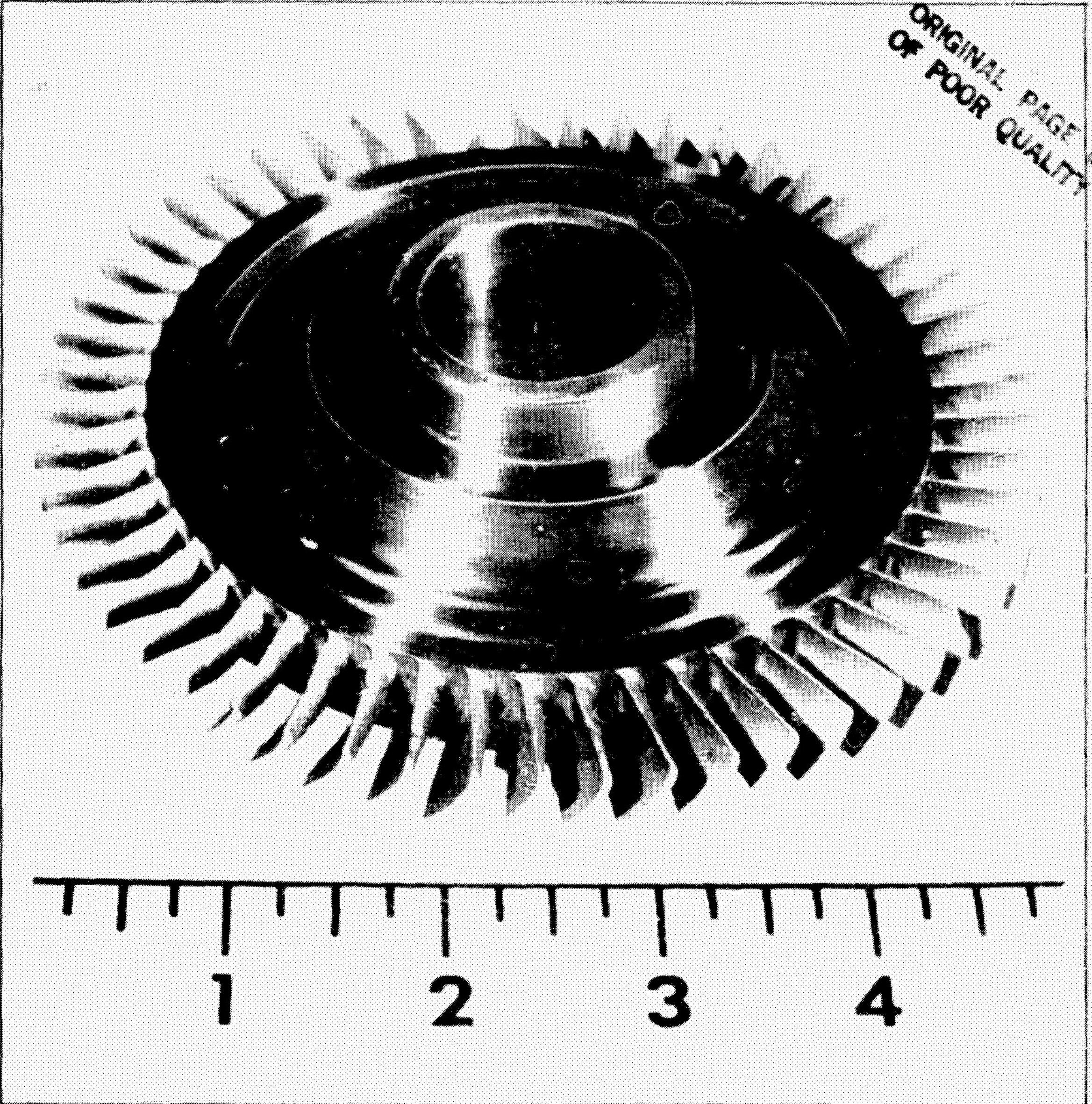

Figure II-9 Turbine wheel fabricated from cast TZM blade ring and forged TZM disk by electron beam welding (Photo courtesy of Climax Molybdenum Co. of Michigan).

disk, is marginal, at best, and may be inadequate. However, higher properties are reported for forged, stress-relieved TZM. A composite wheel comprised of a cast blade ring and a forged hub could offer a suitable combination of properties **(58)**. Such a composite wheel fabricated by electron beam welding a cast TZM blade ring to a forged TZM disk and hub is reported to have successfully withstood limited testing in a simulated engine rig **(59)**. The wheel was protected against oxidation by a modified disilicide coating (W-3). Cast blade ring and assembled wheel are shown in Figures II-8 and II-9. Properties superior to that of forged TZM have been obtained in two experimental alloys: powder metallurgy TZC (PM-TZC) and a hafnium carbide strengthened alloy (MHC) with reported yield strengths, at 1200°C (2200°F), of 580 MN/m^2 (84.1 ksi) and 655 MN/m^2 (95 ksi) respectively, making them suitable disk material candidates **(59)**. The creep behavior of the various alloys is influenced by many factors, particularly alloy content and thermo-mechanical history. Some values are given in Table II-2, and a comparison with the best columbium alloys is shown in Figure II-10.

Fabrication

Ingots of pure and alloyed molybdenum are commercially produced by consumable electrode melting using pressed and sintered powder electrodes. Electro-slag melting has also been used successfully **(44)**. Secondary working is by swaging, forging or rolling depending on the ductility of the alloy and the shape of the end product. Closed die forging is also a commonly used process for repetitive production of simple shape parts. Casting of arc-melted Mo and Mo alloys in graphite lined molds to produce usable castings was done successfully in the early sixties **(55)**. However, precision casting in investment-type molds, suitable

CREEP OF COLUMBIUM AND MOLYBDENUM ALLOYS

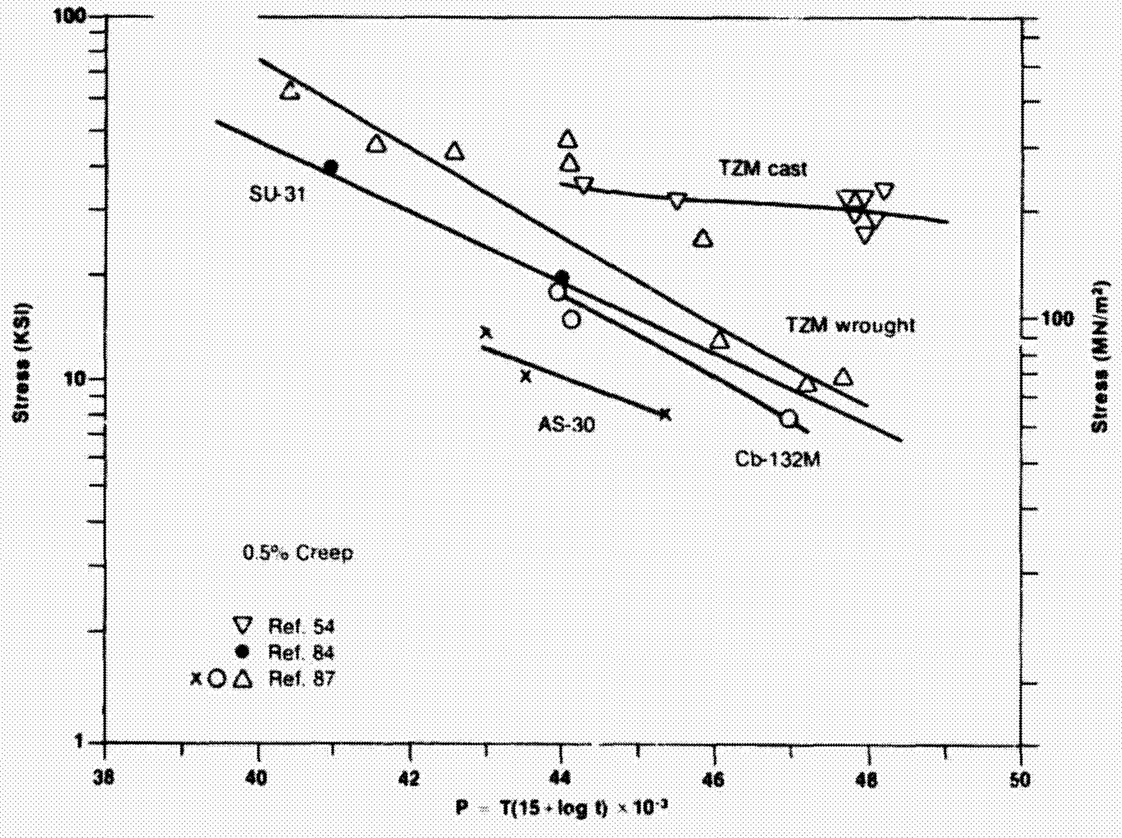

Figure II-10

for producing net airfoil shapes, has been accomplished only recently **(56)**. Integral, automotive size turbine wheels have been successfully cast by this process. (See Figure II-11.)

Most of the common welding processes have been used successfully to join molybdenum alloys by allowing for the unusually high thermal conductivity of the material and its sensitivity to interstitial elements pick-up. Joining of simulated cast Mo alloy wheel hubs to steel shafts by inertia welding has given extremely encouraging results at Chrysler.

Coatings

The poor oxidation behavior of molybdenum is due to the formation of a non-protective volatile oxide MoO_3 **(1)**. It begins to volatilize above 500°C (932°F); at about 770°C (1415°F) the rate of vaporization of the oxide is equal to its rate of formation. Above its melting point, 815°C (1500°F), the oxide runs off the surface and the oxidation becomes catastrophic; rapid failure can then occur due to loss of cross section. Vaporization of the oxide is accompanied by characteristic white fumes. Efforts to improve oxidation resistance by alloying have shown some

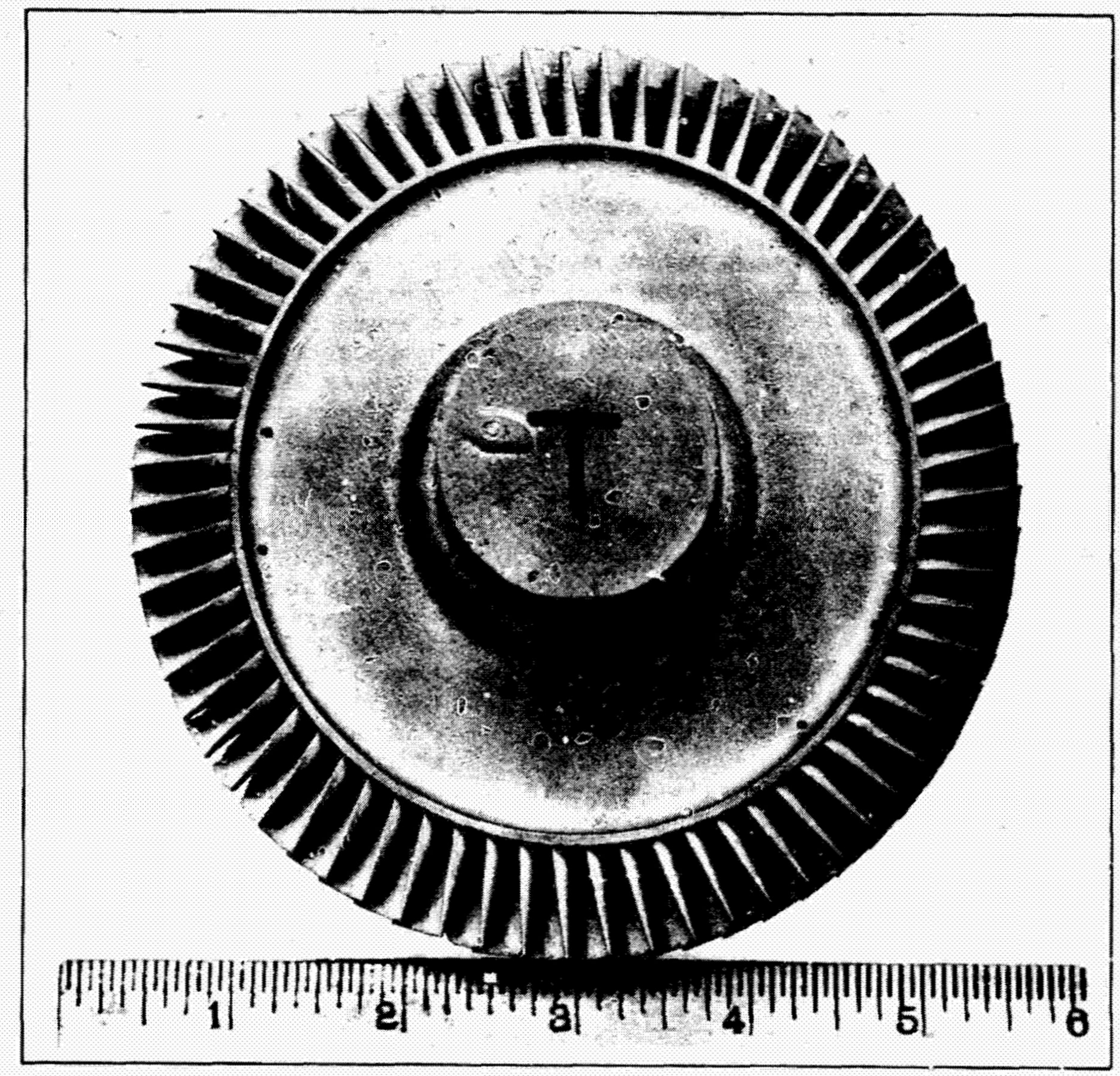

Figure II-11 Investment cast TZM integral turbine wheel. (Photo courtesy of Climax Molybdenum Co. of Michigan).

TABLE II-4
PROTECTIVE COATINGS FOR MOLYBDENUM ALLOYS

Type	Commercial Designation	Supplier or Originator	Process
Cr-Ti Mod. Disilicide	DISIL	Boeing	Fluidized-bed
Cr-Mod. Disilicide	W-2	Chromalloy	Pack Cementation
B-Mod. Disilicide	W-3	Chromalloy	Pack Cementation
Disilicide	Durak B	Chromizing Corp.	Pack Cementation
Disilicide	PFR-6	Pfaudler	Pack Cementation
Cr-Mod. Disilicide	PFR-30	Pfaudler	Pack Cementation
B-Mod. Disilicide	PFR-32	Pfaudler	Pack Cementation
Disilicide	Siliciding	G.E.	Molten salt electrolysis
Disilicide	L-7	McDonnell-Douglas	Pack Cementation

measure of success but the required level of additions is high enough to be detrimental to the tensile properties of the alloys **(60)**. The most promising systems are: Mo-Ni, Mo-Ni-Co, Mo-W-Co, Mo-Cr-Ti, Mo-Ni-Al and Mo-Ca **(52,54)**. They all owe their oxidation resistance to the formation of stable non-volatile molybdates. The commercially available alloys all form the volatile oxides; consequently they require the use of oxidation resistant coatings for atmospheric service at high temperature.

The poor oxidation characteristics of molybdenum and its alloys were recognized early and a wide range of protective systems were evaluated: cladding, plating, metal and ceramic sprayed coatings, diffusion, hot dipping, electrophoresis, etc. **(41,61,62,63)**. Few systems showed much promise and only the disilicide type coatings, in spite of some shortcomings, are still the most commonly used. The basic disilicide coating is formed by interdiffusion of silicon and substrate alloy and consists of several layers of binary compounds (Mo_5Si_3, Mo_3Si, MoSi and $MoSi_2$).

Modification of the binary coatings by addition of Cr, B, Ti, Al or Zr is a commonly accepted practice and is the basis of many proprietary coatings with improved properties **(64,65)**. Many application techniques are used: fluidized bed, pack cementation, CVD, molten salt electrolysis, slurry diffusion etc. Some commercial coatings are shown in Table II-4. Several of the coatings have been developed for aerospace applications where short lives at temperatures as high as 2200°C (4000°F) are a common requirement. The published literature reports mostly test data on coated wrought Mo and Mo-alloy test coupons of simple shape.

Good oxidation test performance has been reported for cast TZM samples coated with a boron modified disilicide (W-3) **(59)**. Samples lasted in excess of 1000 hours in cyclic tests from room temperature to 1100°C (2000°F) and 860 hours to 1200°C (2200°F). But actual service data in an automotive type turbine duty cycle is lacking. Problems are expected at thin sections such as blade trailing edges and at sharp corners where spalling frequently occurs.

Tantalum and Tungsten-Base Alloys

Tantalum and tungsten have the highest melting points of the refractory metal group. Their alloys are relative newcomers in the field and historically their high temperature use has been restricted to temperatures that exceed the maximum useful range (to 1315-1370°C) of the lower members of the group **(66,67,68)**.

High melting point and high strength at elevated temperatures are the attractive features of both metals in the unalloyed condition. Tungsten, with the highest melting point of all refractory metals, 3410°C (6170°F) has exceptional strength (T.S. 10 ksi) at temperatures beyond 1900°C (3450°F) but a high DBTT. Tantalum, on the other hand, has a somewhat lower melting point, 2996°C (5450°F), and lower strength but is extremely ductile, down to sub-zero temperatures (low DBTT ≈ - 195°C, −320°F). The major oxide of tantalum, Ta_2O_5, is relatively stable and very adherent but very porous, which renders the metal susceptible to oxygen contamination and embrittlement at moderate temperatures. Tungsten oxide is nonvolatile up to about 1000°C (1830°F), but even above that temperature, and unlike tantalum, no contamination of the metal occurs with resultant deterioration of properties **(2)**. For extended service at high temperatures both metals require protective coatings.

The high density of both metals and their alloys (16.6 g/cm^3 and 19.3 g/cm^3 for the pure metals) restricts the range of their potential applications.

Strengthening Mechanisms

Strengthening by substitutional solution alloying is effective in both tantalum and tungsten and can provide three to five-fold improvements in high temperature tensile strength. However, decreasing fabricability is produced by high levels of substitutional solutes particularly in tungsten, where the ductility of the pure metal is low (high DBTT) as with chromium and molybdenum. This trend toward lower ductility is accentuated by the high modulus of elasticity of tungsten. Exceptions to the general embrittling effect of solid solution strengtheners are those that promote solution softening ("rhenium ductilizing effect"). Tantalum, with high ductility as a pure metal, is somewhat more tolerant of larger amounts of substitutional solutes and many of its alloys rely solely on that mechanism to provide useful strength at high temperature **(69)**. The commercial alloy T-111, with 8% tungsten and 2% hafnium is a typical example. Precipitation strengthening, on the other hand, is very effective in tungsten as in other metals of Group V A, in increasing elevated temperature properties.

Hafnium carbide precipitation is the preferred strengthening mechanism for tungsten and provides strength enhancement to temperatures as high as 1930°C (3500°F). A carbide content of 0.35 vol% appears to be optimum. Overaging and loss of strength occurs at recrystallization temperature, around 2090°C (3800°F). A slight excess of hafnium appears to have beneficial effects on ductility, probably due to a gettering effect on interstitial impurities. Rhenium in varying amounts is also used in carbide-strengthened alloys for its ductilizing effect on the solution strengthened matrix **(70,71)**. Other carbide formers such as columbium have been studied with some success. Dispersion strengthening with thorium oxide is also used to improve strength while retaining ductility. These alloys are produced by powder metallurgy techniques **(72,73)**. While the principal strengthening mechanism in tantalum alloys is solid solution, some recent alloys gain additional high temperature strength through precipitation/dispersion of carbides **(74)**. Hafnium is used with closely controlled amounts of carbon and the desired strength levels are obtained through varying combinations of suitable thermo-mechanical treatments.

Properties

Temperature capability of typical alloys of both tungsten and tantalum, shown in Figure II-5, appears vastly superior to the other refractory alloys. However, the density corrected figures are more realistic for rotating components and indicate no clear advantage. For static applications outstanding tensile and creep properties are obtained with both families of alloys to temperatures as high as 2200°C (4000°F). A sampling of available properties of tantalum and tungsten-base alloys is shown in Table II-5 **(19,74,78)**.

Fabrication

Tungsten is extracted from its ores by precipitation from solution and hydrogen reduction to pure metallic powder. It is subsequently consolidated by compaction and sintering in hydrogen into a form suitable for remelting and alloying by consumable

TABLE II-5
TENSILE & STRESS-RUPTURE PROPERTIES OF SOME TANTALUM & TUNGSTEN ALLOYS

	1315°C (2400°F)	1370°C (2500°F)	1650°C (3000°F)	2200°C (4000°F)
Tantalum-Base				
T-222				
U.T.S. MN/m²(ksi)	371 (53.8)	—	165 (23.9)	—
100 hr. S-R	193 (28)	—	34 (4.9)	—
ASTAR-811C				
U.T.S.	262 (38)	207 (30)	—	—
100 hr. S-R	—	—	—	—
Tungsten Base				
W-2ThO₂				
U.T.S.	—	— —	203 (29.5)	124 (18)
100 hr. S-R	—	159 (23)	72 (10.5)	—
W-25Re				
U.T.S.	—	—	225 (32.6)	—
100 hr. S-R	—	—	40 (5.8)	—

or non-consumable electrode, or by electron beam. Tantalum can be produced by a similar process but is usually obtained by electrolysis of a fused salt bath. The resulting sponge is subsequently subjected to processing steps similar to those used for tungsten. Primary fabrication by mechanical working in the case of tantalum is relatively easy due to the inherent ductility of the pure metal. In the case of tungsten a protective atmosphere is required, during hot working, to prevent embrittlement by oxygen pick-up. Thorium oxide disperison strengthened alloys are produced by powder metallurgy techniques, by-passing the remelting step.

Coatings

Oxidation resistant coatings for tantalum and particularly tungsten are mostly aimed at a relatively short life at temperatures above 1650°C (3000°F), the range where these metals and their alloys possess outstanding strength. Disilicide coatings are most commonly used with both metals because of their superior thermal stability and compatibility with the substrates. As with other refractory metals, the silicide coating is usually modified by additions to the coating slurry, or by using a pre-deposited substrate in a two-step process. Tungsten, zirconium and titanium have been used successfully as modifiers **(86)**. Tungsten used as a CVD deposited substrate, subsequently pack siliconized, has produced viable coatings on tantalum Some measure of success has also been obtained on tantalum with fused tin-aluminum-molybdenum coatings which depend on the formation of an aluminum oxide layer for oxidation protection. Cermet coatings consisting of a flame-sprayed mixture of chromium and zirconium boride have provided both tantalum and tungsten with adequate short-time protection at temperatures to 2100°C (3800°F) Improvement of oxidation resistance by alloying with hafnium, zirconium and thorium has produced only marginal gains

Cost

The current cost of refractory metals is sufficiently high to cause serious concern regarding their use on a mass production basis such as for automotive turbine engine components. The current market price of the pure metals, compared graphically in Figure II-12, varies from $2.63 per pound for chromium to $45 per pound for columbium. Refractory metal prices have increased at a high rate in the last few years (increases for the period 1969 to 1976 are shown in Figure II-13) and no leveling-off of the trend is foreseen. Although it has been shown that cost and usage of metals are closely interrelated **(79)**, the high cost of the refractory metals (except for chromium) appears due to the inherently costly extraction process from very lean ores rather than to low volume usage, particularly for columbium, tantalum and tungsten **(40,80,81)**. Because of the price interaction of supply and demand even a modest increase in requirements could cause accelerated price increases.

Melting and alloying of the refractory metals require special, more costly equipment and techniques due to their high melting points and their affinity for interstitial elements (nitrogen, oxygen and carbon). In addition, some of the elements most commonly used in the formulation of their alloys, such as hafnium and rhenium, are themselves expensive (hafnium, approx. $50 per pound; rhenium, approx. $540 per pound), further increasing the cost of the alloy melting stock. Secondary processing such as thermo-mechanical treatments under inert atmosphere or hot extrusion of "canned" powders can also add significantly to component cost.

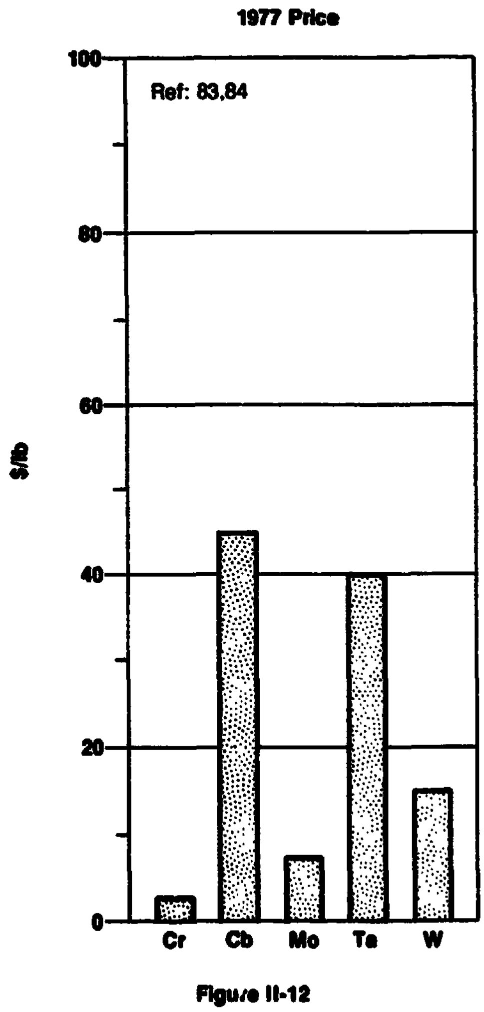

Figure II-12

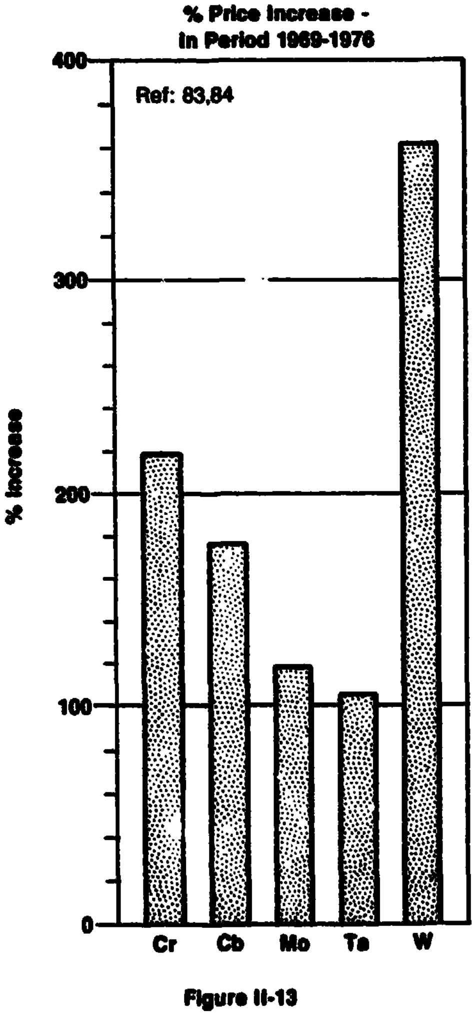

Figure II-13

Replacement of the piston engine by a high TIT turbine engine equipped with a refractory alloy first stage wheel, even in a gradual fashion, could seriously tax production facilities and upset domestic and even world metal markets. At the current production rate of ten million vehicles per year, 7000 tons of chromium (density 7.19 g/cm^3) or 17,850 tons of tungsten (density 19.3 g/cm^3) would be required to replace a 1.5 pound nickel-base alloy compressor turbine wheel. Figure II-14 compares such annual usage to the 1974 U S. consumption of the refractory metals. While the effects of those requirements on the annual domestic chromium consumption might be minimal, the amount of tantalum needed would be over thirteen times the tonnage now used.

Crustal abundance (chromium ranks 21st, columbium 33rd and tungsten, the least abundant of the refractory metals, ranks 59th) **(79)** has little relation to utilization or to richness of the ores. The metal contents and accessibility of individual deposits, or ore bodies, determine the profitability, and thus the geographical location, of tne current supply sources While the United States possesses very large deposits of many industrially important metals, significant quantities of metals and ore still must be imported. Several metals of critical industrial or military importance are almost exclusively imports; among those are columbium, manganese, cobalt and chromium. Domestic availability of the refractory metals is compared in Figure II-15. It is shown to be nil for chromium and

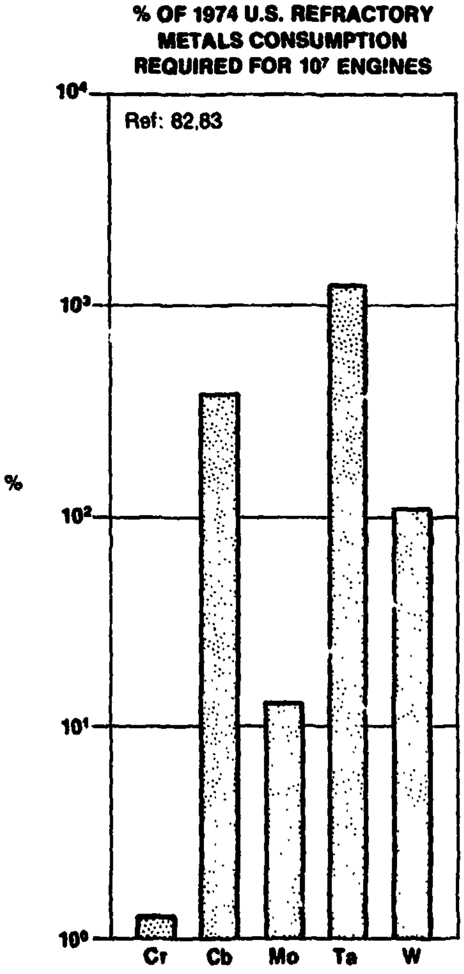

Figure II-14

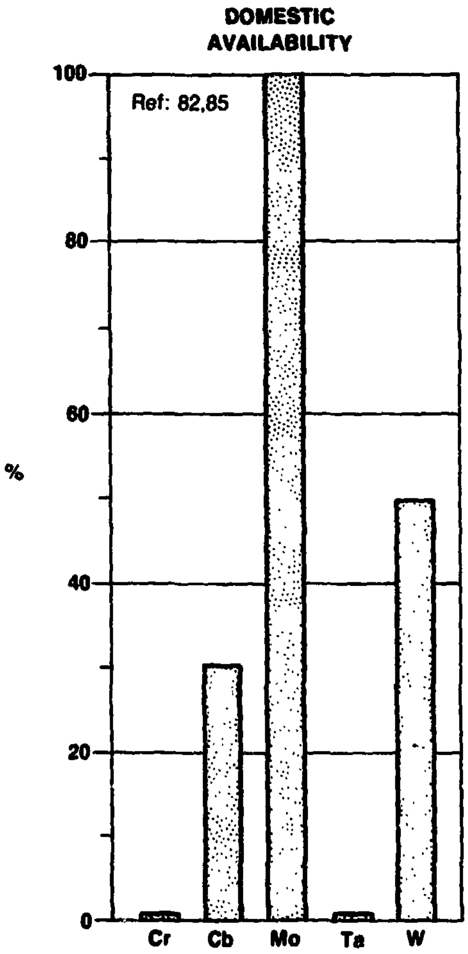

Figure II-15

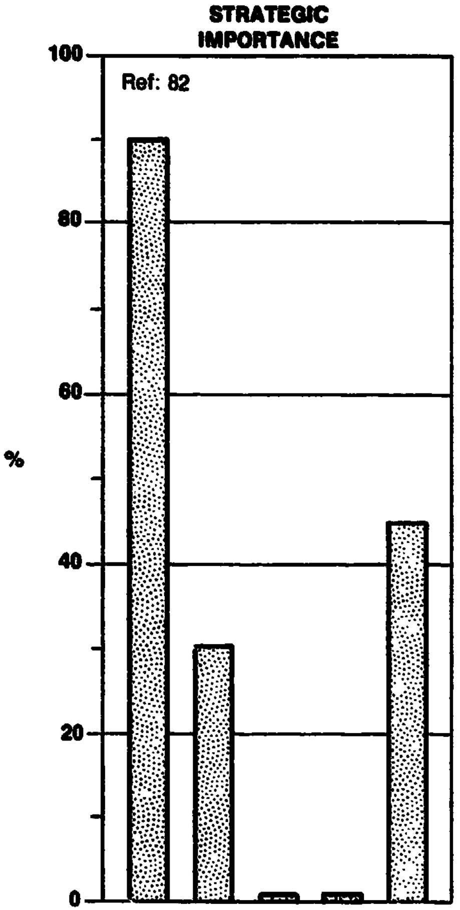

Figure II-16

minimal for tantalum while close to 100% of the current consumption of molybdenum is domestically produced. Cartels already exist among countries with large deposits of petroleum, bauxite, copper, mercury and tin. Others could very easily emerge for some of the refractory metals, with a sudden increase in their demand. The political and economic pressures that such cartels can exert have been amply demonstrated. Present low import volume and free trading of the metals are no assurance of continuing supply at reasonable prices in a future large tonnage market.

A composite ranking of the strategic importance of the refractory metals, on the basis of industrial and national defense requirements, domestic availability and worldwide political considerations (e.g., "friendliness of source countries") is shown in Figure II-16. This ranking is based on several authoritive studies by governmental agencies **(82)**. It graphically emphasizes how the continuing supply of chromium in particular, and tungsten and columbium to a lesser extent, could be at the mercy of worldwide political uncertainties or national emergencies, in spite of the damping effects of current strategic metals stockpiles.

Summary and Conclusions

Selection of a viable material to withstand the severe temperature and stress environment of the Improved Automotive Gas Turbine (IAGT) clearly rests upon careful assessment of properties, cost and availability. The five refractory alloys examined in this report all appear to offer some usable properties for turbine wheel application. However, they all have undesirable features that detract from their potential usefulness, and final selection is at best a compromise.

While tantalum and tungsten have more than adequate stress-rupture strength, their high density would impose unreasonable inertia penalties when used in rotating components. Chromium alloys, on the other hand, would be quite advantageous from the same standpoint, having a lower density than nickel-base alloys, but their extreme brittleness and sensitivity to interstitials preclude their use for such an application. From the standpoint of fabricability, many refractory alloys perform rather poorly. Chromium and tungsten base alloys (Group VI A) because of their low ductility are difficult to reduce mechanically to usable products. Chromium in particular requires extrusion or swaging to gross final shape. Tantalum and columbium on the other hand are very ductile (Group V A) and are readily fabricable although requiring high deformation forces. Molybdenum, while being in Group VI A, has intermediate fabricability. Tantalum and tungsten because of their extremely high melting points, have not been successfully investment cast.

Although alloys of both columbium and molybdenum are normally used in the wrought condition, several of them have recently been investment cast with extremely encouraging results. The experimental shapes produced include small integral turbine wheels and commercial engine size airfoil shapes with acceptable surface finish. In view of the small size of the projected turbine wheel, precision investment casting to net shape appears to be the only currently practical method of secondary fabrication.

In the event that the final material choice for the hot gas path components of the IAGT is a refractory alloy, raw material cost will be an important consideration in mass production decisions. While the relative low cost of chromium is undoubtedly attractive, some alloy development breakthroughs are required before full advantage can be derived from that alloy system. At the other end of the scale, the high cost of tantalum coupled with a high density precludes serious consideration of its use as a compressor turbine wheel material. Tungsten-base alloys are of intermediate cost but have a high DBTT.

The base materials for the castable refractory alloys, columbium and molybdenum, are practically at opposite ends of the cost range, with molybdenum second only to chromium. This cost advantage holds not only for the pure metal but also for the commercial alloys which contain less than 2% additions. Availability and strategic importance, while not the primary selection criteria, strongly favor molybdenum in view of its ample domestic reserves and production capac''

The stress-rupture properties of the various molybdenum and columbium alloys cover essentially the same range and the selection is usually governed by fabricability. In a cast turbine wheel, where property optimization by thermo-mechanical treatments is not feasible, the actual properties are expected to be in the range of recrystallized or stress-relieved alloys and will be affected by process variables. The properties of the cast columbium alloys are reported to be comparable to that of the wrought material (with similar thermal history); actual test results show cast TZM to be somewhat superior to the stress-relieved wrought alloy.

The creep properties of molybdenum alloy TZM, cast and wrought, are also superior to that of the strongest columbium alloys. While molybdenum alloys appear to be the best suited of the refractory alloys for the proposed high TIT automotive turbine engine compressor wheel, they have one common serious deficiency: a catastrophic oxidation behavior. In spite of that problem they remain extremely attractive because of their unique hot strength. The oxidation problem is partially alleviated by the use of protective coatings. However, serious consideration of the usage of molybdenum alloys in the IAGT would require additional development efforts particularly in the area of coating reliability.

C. Belleau
January, 1978

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Section III

Ceramic Materials

Section III - Ceramic Materials

Introduction

For prolonged service at potential turbine inlet temperatures (TIT) of 1370°C (2500°F), it has been established that nickel and cobalt based superalloys are not capable of survival. Incipient melting, beginning at metal temperatures near 1200°C (2200°F) requires that the TIT be limited and necessitates the use of sophisticated, inefficient air cooling. Refractory metals, as a group, exhibit two serious deficiencies - a poor resistance to oxidation, thus making the use of protective coatings imperative, and a high ductile-to-brittle transition temperature (excepting Cb and Ta). Other general disadvantages of the refractory metals are undesirably high density (high inertia weight of rotating components), and potential cost and availability problems.

Focus in recent years has turned toward ceramic materials, specifically Si-C and Si-N based, as the only practical alternatives capable of continuous 1370°C (2500°F) uncooled operation; the efficiency benefits accrued from such high temperature operations have been widely publicized. The selling points which inherently characterize ceramics for high temperature operation include, but are not limited to, high oxidation/corrosion resistance, high creep resistance, relatively low density (compared to metals), and low raw materials cost. Despite these celebrated advantages, it is common knowledge that ceramics, by nature are brittle materials; i.e. they have a low fracture toughness (K_{IC}). Because of this factor alone, ceramics have, to date, met with limited success in such highly stressed applications as turbine rotors, although numerous material development and design programs have been undertaken to confront this problem. In recent years, sophisticated finite element computer analyses have proven themselves invaluable as a design tool for predicting stress concentrations and probabilities of failure. Nevertheless, it must be remembered that ceramics technology (for gas turbine application), and more specifically brittle materials design, are at an infant stage of development. To date, we are still climbing the steep side of the technological learning curve. Static ceramic parts, however, have been successfully implemented within the hot zone of the automotive gas turbine by industrial researchers. The highly stressed, high rotational speed rotor has been and remains to be the prime focus of attention. Great progress is being made toward the goal of a durable, functional, all ceramic wheel capable of withstanding an inlet temperature which may go as high as 1370°C (2500°F).

The purpose of this literature review is to consider the available candidate ceramic materials (particularly SiC- and Si_3N_4-based) and evaluate the use potential of each for specific parts, both static and dynamic. Regenerator materials are also reviewed along with an analysis of coatings, joining methods, machining methods, and economics of various ceramic raw materials and processing techniques.

Throughout the writing of this review, special consideration has been given to the reading audience. The two-fold aim of this work is that it might be enlightening to both the experienced materials researcher, and to the responsible administrator who so very often finds himself accountable for the decisions made regarding material development and selection. If there must be one criticism of this work, let it be that it is directed too far toward that imaginary point representing the center of the "overlap of influence band", which ties together these two discrete groups.

Ceramic Material Candidates

High Stress, High Temperature Parts

One factor that can be directly related to the ultimate strength of a ceramic material is density; in general, strength has been found to increase with increasing density (Fig. III-1). For a ceramic material to exist as a nozzle or a rotor in the extreme environment of a gas turbine engine, it will need to be essentially 100% theoretically dense (in addition to satisfying the other necessary requirements, i.e. high strength at high temperatures, low thermal expansion, high creep and oxidation resistance, cost/availability, etc.). The following section is an overview of the present technology of high density material for gas turbine engine application and their fabrication techniques.

Hot Pressed Silicon Carbide

Even under pressure, densification of coval[illegible] bonded solids such as BN, SiC, Si_3N_4 and [illegible] condition is extremely difficult **(1)**. It has been shown that addition of sintering aids to the pure powders acts to form a liquid phase which dissolves the SiC to promote densification by a solution-reprecipitation mechanism **(2)**. Hot pressed SiC is produced by combining high purity, fine mesh SiC powder with small amounts of a sintering additive (usually 0.5 - 5 wt.% MgO, Al_2O_3, Al, B, Fe or B_4C). The mixture is then pressed at high temperature to a billet of full density using graphite dies and plungers. Hot pressing parameters normally used are temperatures of 1750° to 2000°C (3160° to 3630°F) and pressures of 20 to 40 MN/m^2 (3 to 6 ksi) for a few minutes to an hour.

The billet, thus produced, is then either diamond or electrical-discharge machined (EDM) to its final configuration (See Machining methods). Although parts produced by hot pressing can attain theoretical density, expenses incurred in die tooling and final machining make the technique prohibitive for mass production of complex parts. Components manufactured with complex shapes must be formed to near final shape without machining to minimize cost **(3)**.

Hot pressing yields high strength material at room temperature, however the strength of most HP SiC (and Si_3N_4) decreases dramatically at elevated temperatures (Fig. III-2). Subcritical crack extension via grain boundary sliding is the phenomenon responsible for this strength degradation **(4)**. Sintering aids and impurities such as CaO tend to decrease the viscosity of the grain boundary phase (the hypothesized silicate phase) at high temperatures **(5)**. For the same reason, compared to other SiC candidate gas turbine ceramics, this material exhibits a high creep rate (a measure of the deformation of a material under constant stress) in high temperature environments. Current research on hot pressed SiC aims at improving the high temperature strength and creep resistance of the material by controlling starting powder impurities and experimentation with different sintering aids. It is Chrysler's contention, however, that for large scale production of complex parts such as rotors and vanes for an automotive gas turbine engine, hot pressing of SiC is unsuitable because of high capital investment, low production rate, and high tooling and machining expenses.

CERAMIC MATERIAL STRENGTH VS. DENSITY

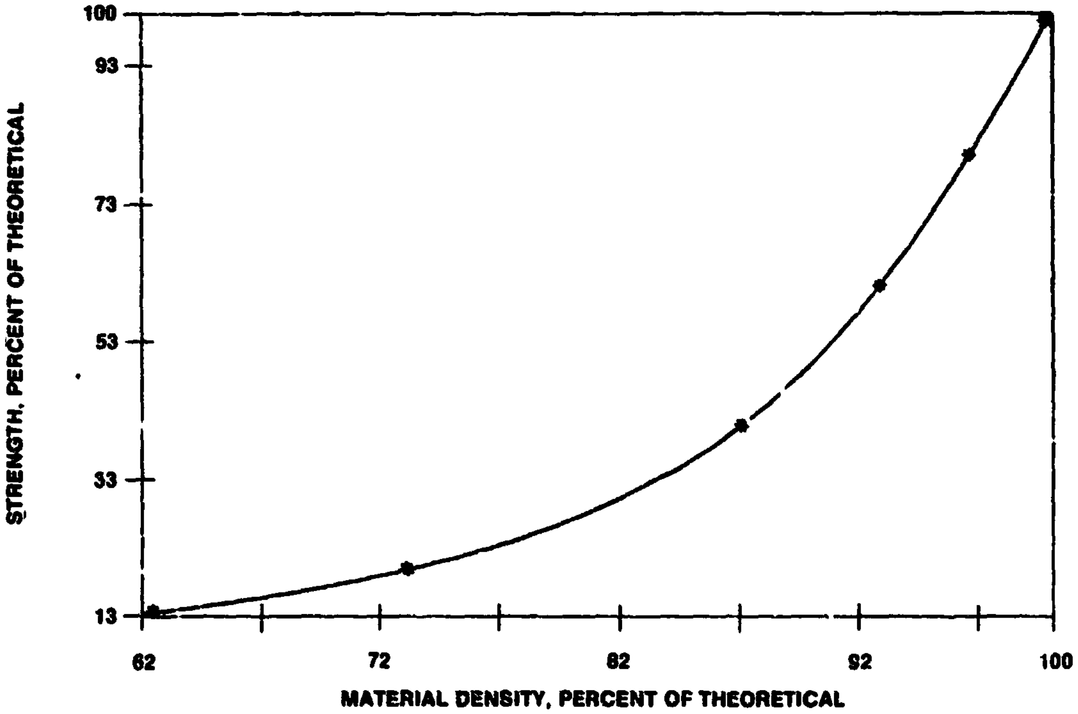


Figure III- 1

Chemical Vapor Deposited Silicon Carbide

Chemical Vapor Deposition (CVD) is another method of attaining dense (greater than 99% of theoretical) silicon carbide. The CVD process entails directing gases containing the constituent elements of the desired final material onto a heated substrate of selected composition and geometry. During impingement, sufficient thermal energy is transferred to the gases to activate a chemical reaction which produces the intended product as a solid. This solid product is deposited as a coating on the substrate one molecule at a time. This is a continuous process which is maintained until a coating of sufficient thickness is formed. After deposition, the solid coating may be left on the substrate or the substrate may be removed by etching or burning to leave a homogeneous body (6).

Thus, ceramic materials may be formed "as deposited" by CVD into the final turbine rotor shape. The method is very similar to investment casting except that the part is formed by "pouring" gases rather than liquid metals (7). Early work done by the Energy Research Corporation, under subcontract to Ford (8), resulted in fabrication of a single turbine blade and complete first stage rotor. This rotor, while far from ideal because of poor material quality, lack of complete filling of the blades, and incomplete removal of stresses formed during deposition, is considered a demonstration of the feasibility of fabricating a full turbine rotor shape from CVD silicon carbide (8).

Other fabrication processes have been developed to produce CVD ceramics (7). However, this material has exhibited both gross and microscopic cracking problems that have prevented the routine production of thick, sound, parts. Currently, it is possible to produce parts with thicknesses up to 1.6 cm (5/8") with low flaw density. The present work is directed at reducing the flaw size and flaw density so that high quality material can be consistently produced. To date, the quality of the rotor part has not reached the quality level warranting a full scale testing program under thermal or rotational conditions. The principal effort has been directed to

STRENGTH VS. TEMPERATURE - CERAMIC MATERIAL CANDIDATES

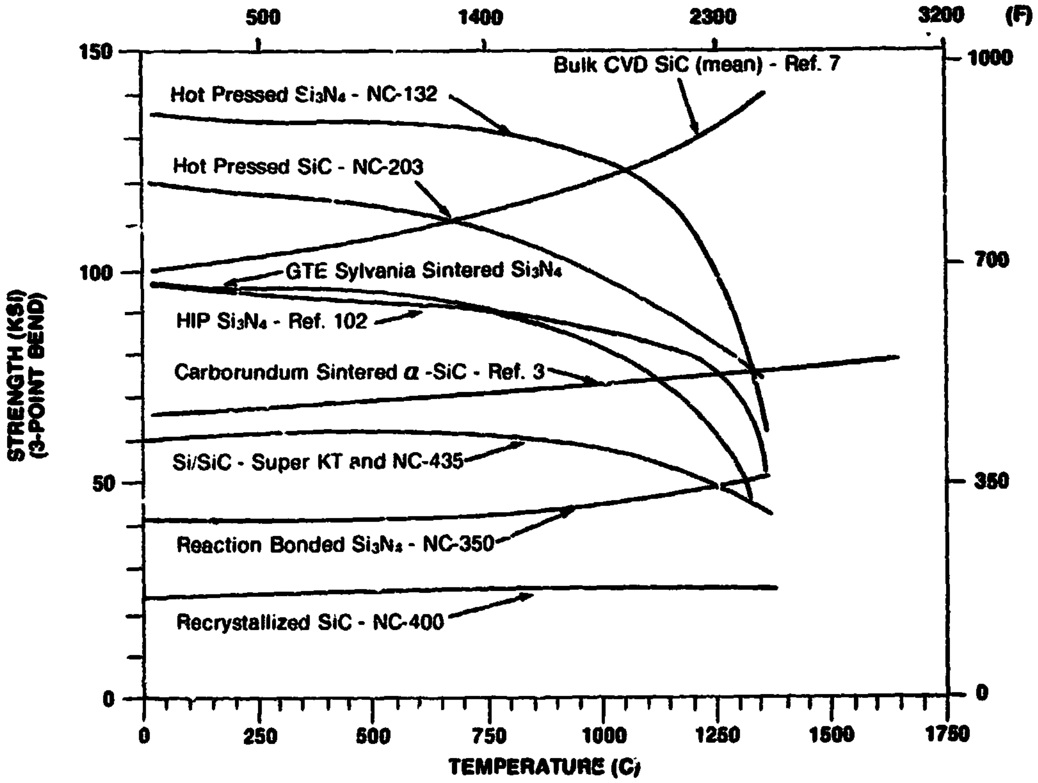


Figure III - 2

the design, fabrication, and material technology areas that would lead to a product justifying the expense of application testing.

Removal of residual stresses in the deposited material is the major problem encountered in the CVD fabrication process. These are defined as the stresses remaining in the material after making allowance for the thermally induced stresses **(9)**. Stresses in CVD materials arise in two ways: the first is by mismatch of thermal expansion between coating and substrate, which can be calculated from the expansion coefficients. These can be reduced with a suitable choice of substrate. The second is by thermal rearrangement within the coating, either during or subsequent to deposition **(9)**. The aim of researchers is to minimize these stresses so that cracking does not occur in the finished part.

Despite these fabrication problems, CVD silicon carbide is an attractive candidate for turbine service because it has demonstrated high strength at elevated temperatures (Fig. III-2), it is a high density product, there is minimal final machining necessary, it can have a surface finish equal to that of the original substrate, and it has low creep and oxidation rates

Sinterable Silicon Carbide

A significant advancement in producing high density silicon carbide has recently been announced separately by the General Electric Company and the Carborundum Company. These methods involve mixing submicron SiC powder with small amounts of an additive, forming, and sintering without pressure to densities greater than 98% of theoretical The feasibility of pressureless sintering of SiC implies that most of the conventional forming and processing procedures developed for ceramics may be applied to SiC to produce dense bodies of complex shapes

In 1973 researchers at the General Electric Company announced the pressureless sintering of beta SiC powder **(10)**. Sintering, in this case requires the use of small amounts of solid solution additives and the application of reducing atmospheres during the sintering process. The preferred dopant is boron at concentrations slightly higher than the solid solubility of boron in SiC ($\approx$0.3 wt%) at a sintering temperature of about 2100°C (3800°F). Reducing conditions are generally obtained by the use of 0.5 to 1 wt% free carbon mixed with the starting powders **(11)**. Prolonged sintering time, impurities, or the use of excessive temperature often promotes an undesirable nucleation and transformation of beta to alpha - SiC.

A processing and firing schedule has been developed, however, which will consistently yield fine grained β-SiC. This procedure necessitates the use of extremely phase-pure β-SiC powder to which all unnecessary metallic impurities are carefully avoided **(11)**.

The Carborundum Company announced the development of pressureless sintered alpha - SiC in June, 1976 **(12)**. Sintering can be performed over a range of temperatures; 1900°-2400°C (3450°-4350°F), in a variety of environments, e.g. argon, nitrogen, helium, or vacuum. The higher temperatures can readily be used with this system since the transformation problems associated with β-SiC above 2100°C (3800°F) are avoided. The submicron powder used in the process is an Acheson-furnace product consisting entirely of α-SiC and, as produced, is of a purity level which requires only the addition of sintering aids **(12)**.

The forming techniques for sinterable SiC are not unlike those of more common ceramic materials (with slight modifications), and include die pressing, slip casting, injection molding, extrusion, compression molding, and prefired machining. These forming techniques have advantages and disadvantages depending on the desired final shapes. Generally, the production of these shapes requires the use of various binders, lubricants, and various powder forming vehicles which may affect the processing results.

Die Pressing: *For relatively simple shapes such as bars, rods, etc. this forming technique is perhaps the simplest. The dry powder can be uniaxially pressed in a die, or with an organic binder, then sintered. If a binder is used, a low temperature burnoff is necessary before final firing Final densities usually vary between 96-97% of theoretical as a result of uniform linear shrinkage of about 17-19%.*

Slip Casting: *This forming process is particularly suitable for the production of hollow shapes of multiple curvature. The powder is suspended and dispersed in an aqueous slip, then poured into a plaster mold of the desired shape. As the plaster "pulls" the water out of the slip, a layer of material builds up against the mold. When the desired wall thickness is attained, the mold is inverted and the remaining slip poured off. The remaining part is air dried, then sintered. Some slips respond to pH adjustment, while others require a small addition of sodium silicate as a dispersing agent. Sintered structures of 92-95% theoretical density are possible. Slip casting, followed by pressureless sintering is the only known procedure for producing a dense ceramic of this shape.*

Injection Molding: *This technique is especially appealing for producing complex parts such as turbine blades or rotors. The process utilizes various hot waxes as the carrying vehicles for the SiC powder. Pressures of the order of 3.5 - 6.9 MN/m² (500-1000 psi) are adequate for the die filling process. Upon solidification, the wax imparts sufficient green strength to the article for its removal and subsequent handling. Prior to firing at high temperatures for densification, a relatively low temperature furnacing at about 200°C (390°F) for a specified time is required to remove most of the wax from the structure* **(11)**. The mold must be designed larger than the desired part size to allow for uniform linear shrinkage of about 18% *(approx. volume change of 40%) during final sintering* **(12)**.

Extrusion: *It is possible to produce continuous extrusions of SiC when mixed with a wax vehicle. The process may be regarded as a variation of the injection molding process Dewaxing and firing procedures are similar to those of injection molding.*

Prefired Machining: *If machining is required during the fabrication of a structure of sintered SiC, the machining may be done with considerably less difficulty in the prefired state. The prefiring operation involves firing at 1600° - 1800°C (2900°-3270°F) to a linear shrinkage of 1-5%, thus producing sufficient strength for gripping and machining. In this prefired state, SiC machines easily with bonded SiC grinding wheels. The final sintering step results in a desnsity of 93-98% of theoretical* **(11)**

In the future, it is entirely possible that those desirable properties of high density silicon carbide, i.e. high strength at elevated temperatures, low thermal expansion coefficient, high thermal conductivity, and superb creep resistance may best be realized by sinterable SiC. Researchers at General Electric and Carborundum are continuing efforts to boost material strength levels even higher by eliminating large, scattered pores caused by particle agglomeration during firing. The full strength potential of sintered SiC will not be realized until such flaws are eliminated.

The question of raw material availability is an important consideration. Currently there is no large commercial source of β-SiC powder used for producing General Electric sintered SiC, whereas Carborundum is now producing SiC at low tonnage levels and is constructing a facility for processing tonnage quantities of sinterable SiC powder into prototype shapes and parts **(12)**. Commercial availability will be a critical factor in determining which form of sinterable SiC, alpha or beta, will achieve the most widespread use.

Hot Pressed Silicon Nitride

In recent years much research has been expended toward developing and improving hot pressed silicon nitride for use in the gas turbine engine. The procedure for hot pressing silicon nitride is very similar to that for hot pressing silicon carbide, except for a difference in sintering additives. MgO, in concentration of 1-5 wt% has been the most frequently used densification aid, however high creep and oxidation rates at temperatures greater than 1200°C (2200°F) have prompted studies toward other additives. An additive such as zircon ($ZrSiO_4$) which both promotes densification and forms a more refractory silicate grain boundry phase has been proposed **(13)** and tested **(14)** along with ZrO_2, ZrN, and ZrC (3 wt%). The oxidation rate constant was an order of magnitude lower than those for other hot pressed silicon nitrides produced according to the current "state-of-the-art", e.g. at 1500°C (2732°F), 4.98×10^{-4} $mg^2cm^{-4}min^{-1}$ for the Zr^{4+} additive vs. 2.74×10^{-3} $mg^2cm^{-4}min^{-1}$ for a MgO additive **(14)**. A manufacturer has also hot pressed high purity Si_3N_4 powder with a 4 wt% ZrO_2 (Y_2O_3 stabilized) additive to nearly theoretical density. In 100 hour stress-rupture tests at 1324°C (2410°F) and 103 MN/m² (15 000 psi), this product exhibited better creep resistance than dense hot pressed samples containing 1 and 4 wt% MgO as an additive **(14)** (57 h life vs. 42 h and 34 h lives for the MgO samples, respectively). It also appears that Zr may have a beneficial effect not only when it is used as the sole hot pressing aid but also when a significant concentration of Mg is present in the matrix material **(15)**.

An Si_3N_4-Y_2O_3 composition has been developed which yields markedly improved high temperature properties, without showing intermediate temperature deterioration common to many Si_3N_4 materials using Y_2O_3 as a hot pressing additive **(16)**. The resultant high temperature properties of these products are improved considerably compared to HP Si_3N_4 with MgO additions. Enhanced high temperature strength, which appears to be purity dependent to a certain extent, results from the formation of a yttrium-silicon oxynitride phase at the grain boundaries. A minimum amount of Y_2O_3, generally 5-10 wt%, appears to be required to complete formation of the oxynitride boundary phase and produce significant improvement in high temperature properties. Further studies on resistance to oxidation, impact and thermal shock are being pursued at this time **(17)**.

The Ford Motor Company, sponsored by the Advanced Research Projects Agency has been working to development ceramic components, including the highly stressed turbine rotor, and demonstrate them in a 200 HP size high temperature vehicular gas turbine engine **(18)**. The attainment of this objective will be demonstrated by 200 hours of operation over a representative duty cycle at turbine inlet temperatures of up to 1370°C (2500 F). Ford has done pioneering work on an approach to making duo-density turbine rotors in three pieces. In this concept, a pre-formed hot pressed silicon nitride hub is hot press bonded to a reaction sintered silicon nitride blade ring by means of a separate bonding ring of hot pressed silicon nitride (with MgO additive). The advantages to this system are reduced damage to the blade ring because of lowered hot pressing forces, and greater flexibility in the fabrication of the center hub since it is formed in a separate operation. Preliminary hot spin test results were encouraging, however failures at the hot pressed hub have continued to occur.

To date, a successful ceramic turbine rotor has not been made from any material by any fabrication technique. Even if a successful prototype duo-density rotor could be made using hot pressed silicon nitride, it is extremely doubtful that the process could be made economical for large scale production. The graphite dies used for hot pressing are very elaborate and would incur large tooling costs. Machining the pressed billets to a complex shape would add additional costs.

There is one small bright spot, however. There has been some success **(19)** in hot pressing Si_3N_4 powder to the shape of a turbine vane, maintaining the desired contour tolerances and surface finish. As-pressed contours would eliminate much of the expensive diamond grinding now required for such hardware. Although the technique requires much more investigation, these researchers feel that hardware with a shape of this general type could feasibly be manufactured at a reasonable cost. Unless a method such as this can be made feasible to produce hot pressed parts to shape, economically speaking it will be highly unlikely that any future mass produced ceramic turbine engine will contain a hot pressed rotor.

Sinterable Silicon Nitride

Until recently, silicon nitride components could be produced via two main routes, namely by reaction sintering and hot pressing. Reaction sintered products, although produced by conventional, well-tried fabrication techniques, have a high porosity (about 20%) and therefore an insufficient strength for highly stressed turbine components. Hot pressed parts have good strength and thermal properties, however the required complex forms must be cut from hot pressed blocks using diamond or ultrasonic machining. These are costly processes and do not lend themselves to volume production. Thus it would be highly desirable to use the lower cost, high volume fabrication methods of traditional ceramic processes (such as described for sinterable silicon carbide) to produce Si_3N_4 components having properties and densities approaching those of hot pressed Si_3N_4 **(20)**.

Pressureless sintering is an attractive route toward achieving this goal. Densities 95% of theoretical **(20,21)** and greater have been reported for this material by researchers. Currently, a commercially available sintered Si_3N_4 (GTE Sylvania SN-2502) is available with 98% theoretical density. The reported strength properties for this material vs. temperature are described in Fig III-2.

MgO, Y_2O_3, and CeO_2 are the most favorable sintering aids for producing sintered Si_3N_4. Temperatures of 1500°-1700°C (2730° - 3100°F) are normally used under 1 atm. of N_2 for 15 minutes to obtain 90% theoretically dense materials. To obtain densities greater than 95% theoretical, higher temperatures of 1700° to 1950°C (3100° to 3540°F) must be used. At temperatures greater than 1700°C (3100°F) thermal decomposition becomes significant and conversion of Si_3N_4 to SiC takes place at the sample surface because of the graphite heating elements **(20)**. For this reason, sintering done at higher temperatures must be done under N_2 or Ar pressures of 0.7-2.0 MN/m^2 (100-300 psi).

Using high purity Si_3N_4 powders + 20 wt% CeO_2 a specimen with bulk density of 3.50 g/cm^3 (fully dense) produced 4-point modulus of rupture values of 365-435 MN/m^2 (53 to 63 ksi) at room temperature **(22)**. MOR values at 1316°C (2400°F) obtained in Ar for specimens from this fully dense compact were 372-386 MN/m^2 (54 to 56 ksi) **(22)** indicating little, if any strength degradation at high temperatures. Sintering temperatures were 1950°C (3540°F) at a N_2 pressure of 2 MN/m^2 (300 psi) **(22)**.

Densification of Si_3N_4 by sintering can be accomplished by basically simple means after the conventional forming methods are utilized, i.e. slip casting, injection molding, extrusion, etc. Properties now being reported are by no means the ultimate possible for this material. In the near future, as improved temperature and pressure optimization parameters are developed, and more attention is paid to powder size and purity, densities greater than 98% of theoretical are expected **(23)**.

Hot Isostatically Pressed Silicon Nitride

Perhaps the most promising fabrication method for producing dense silicon nitride parts to shape is hot isostatic pressing (HIP). Simple, 100% dense shapes with high strength can be produced by conventional hot pressing of Si_3N_4 + additives. Complex shapes of 95-98% theoretical density can be produced by sintering with use of additives to give material strengths 70-80% that of hot pressed Si_3N_4. The HIP technique permits complex shapes typical of sintered processes to be economically produced with strengths comparable to those of hot pressed Si_3N_4.

Hot isostatic pressing is a process in which a high gas pressure is exerted on an encapsulated powder mass at elevated temperature. As pressures of 100-300 MN/m^2 (15,000-50,000 psi) are applied from all directions, most ceramic materials can be consolidated to virtually pore-free bodies at only 0.5-0.8 of their melting temperature **(24)**. Maximum allowable chamber pressure is, of course, governed by the working temperature.

Silicon nitride powder is first mixed and milled to the desired particle size. Necessary sintering aids may also be added although the amount may be reduced substantially compared to what is needed for the hot pressing process **(24)**.

A green powder body can be made by two general techniques: (1) Conventional forming, i.e. slip cast, extruded, injection molded, die pressed, etc. In this case, molding is usually accomplished with the aid of an organic binder which must later be burnt off. The preferred technique of forming a dense green body is by (2) cold isostatic pressing. The mixed and milled powder is, in this case, put into a rubber capsule mold and compacted at pressures up to 600 MN/m^2 (85,000 psi). The compact thus produced is of sufficient green strength that any machining necessary may be done prior to the HIP process.

The dense powder body has an open (connected) porosity which makes it necessary to apply a temporary barrier to high pressure gas infiltration before hot isostatic pressing. The compact can be placed inside a molybdenum can encircled with heaters **(25)**. Pressure can be applied to this system via a gas (gas hot isostatic pressing) or the system can be surrounded in sand encased in a metal bag. Water, up to 415 MN/m^2 (60,000 psi) can be used to press against the bag of sand (hydraulic HIP). Using these particular techniques Si_3N_4 has been consolidated to 95% theoretical density without additives **(25)**. Sealing of the metal containers remains a problem with this technique, as the can tends to buckle, crack, and leak.

Another even more promising method of densifying the powder compact is to place the body in an oversize container of silica or borosilicate glass **(23)**. The capsule is evacuated at an elevated temperature before sealing off. During the first phase the temperature is increased to the softening point of the glass. Pressure and temperature are increased to the final operating values, 1700-1800°C (3100-3270°F) and 100 MN/m^2 (14,500 psi) for an hour or more The preformed part shrinkage is totally uniform and predictable. The glass capsule is removed after the HIP cycle by sandblasting or by thermal shocking.

Carrying the glass encapsulation one step further, it has been possible to spray a glass frit onto a preformed (cold isostatically pressed) compact invacuo. This eliminates forming an oversize "milkbottle" container for the part, evacuating, then sealing. This method has been found to be economical, and has resulted in Si_3N_4 specimens with exceptionally high strengths **(26)**.

Mechanical properties of HIP Si_3N_4 *are better than* Si_3N_4 produced by any other forming method. Because such a small amount of sintering aid is needed to prepare fully dense specimens, there is less strength degradation than HP Si_3N_4 at high temperatures due to intergranular low viscosity phases (Fig. III-2) Furthermore, fully isotropic, dense silicon nitride is obtained using the HIP process. This is not the case with hot pressed silicon nitride, where strengths in one direction may be 20-25% weaker than in another direction. HIP Si_3N_4 has the same high strength in all directions as hot pressed has in the strongest direction **(102)**.

Even more important than the mean strength of a material is its Weibull modulus (m-value). This is a measure of the degree of variation in strength of a *material over a given sample population. Ceramic* materials with m values greater than 10 are considered to be good technical ceramics. Most ceramic materials fall into a category of 3 to 8 However, "m" values of 20 with a mean strength of 900 MN/m^2 (130,000 psi) and m values of 40 with a *mean strength of* 760 MN/m^2 (110,000 psi) at room temperature have been reported for HIP silicon nitride **(26)**. These numbers are by far the most encouraging that have been reported to date. Based on these preliminary results obtained on simple shaped test bars it would appear that hot isostatic pressing of silicon nitride may turn out to be the most viable solution to the problem of fabricating a working ceramic turbine rotor in the near future.

Medium Stress, High Temperature Parts

Most parts in an all ceramic gas turbine engine will not be exposed to the extreme mechanical and thermal stresses of the turbine wheel rotors or the nozzle, and will not require such high density, high strength materials. Such parts include the mixer, burner tube, vortex, vanes, struts and shrouds. For *these applications recrystallized and reaction* bonded silicon carbide, reaction sintered silicon nitride, Si/SiC composites and possibly Si-Al-O nitrides (SiAlON) are prime candidates.

Recrystallized Silicon Carbide

Recrystallized, or direct bonded silicon carbide, is produced by firing a "green" preformed compact of fine SiC powder in a reducing gas atmosphere at temperatures near 2250°C (4082°F) causing a change in crystal structure by increasing the size of the smaller crystals and bonding them to the larger **(28,29)**. A commercial grade of this material, known as Crystar or NC 400 is available from the Norton Company. This material contains approximately 18% porosity, consequently it does not exhibit exceptional strength. Nevertheless, strength does remain constant (Fig III-2) to over 1400°C (2552°F), making recrystallized SiC a viable candidate for medium stressed, high temperature structural application.

Recrystallized SiC can be fabricated by conventional ceramic forming techniques (Crystar is slip cast) into complex shapes, and can be coated with an impervious layer of silicon carbide by chemical vapor deposition to improve strength and oxidation characteristics **(28)**.

A method of high pressure slip casting has been developed **(30)** which may, in the future, be suitable for mass production of slip cast products. Using this technique, greatly increased casting rates are achievable, and casts of unlimited thicknesses can be formed compared to conventional slip casting where maximum thicknesses of only 2 cm (=0.8") are attainable. Using this technique, a porous plug of silicon carbide is used in place of the plaster mold, and hydraulic pressure is applied. Thus the use of temperamental plaster of Paris can be eliminated allowing tighter tolerances to be held on the finished product Recrystallized silicon carbide is well suited for production by this method, if chosen for use in an all ceramic high temperature turbine engine.

Reaction Bonded Silicon Carbide

A number of different forms of reaction bonded silicon carbide are currently available This process for producing SiC has been in existence for nearly twenty years **(12)**. In this process, silicon carbide grain is mixed thoroughly with graphite (carbon) and an organic binder and formed by one of several standard techniques into a "green" body. The methods of extrusion, transfer molding **(31)** (utilizes a thermosetting binder) or injection molding (utilizes thermoplastic binder), slip casting, isostatic pressing and uniaxial pressing are being developed for complex shape fabrication. The "green" body is then cured and fired to drive off the volatiles. High temperature infiltration with liquid silicon causes a reaction with the carbon present to form SiC, thus bonding the existing SiC grains together. Excess free silicon fills the voids which result when lower density carbon and silicon react to form SiC. The result of this process is a matrix consisting of pre-existent SiC grains bonded together by reaction product SiC with isolated regions of free Si **(3)**.

A few commercial grades of reaction bonded SiC that have recently received much attention are Refel, NC-430 and 435, and KT and Super KT. Refel, sold by British Nuclear Fuels Ltd., contains primarily 12 μm α-SiC grains bonded together with β. It is essentially pore free and contains 8-10 vol% silicon **(29)**.

Norton's NC 430 is a recrystallized body having the small amount of inherent porosity filled with silicon (6 to 13 vol%). It is basically a silicon densified form of recrystallized SiC (NC-400) but has improved strength properties over NC-400. Interestingly enough, there is little difference in cost between NC-400 and NC-430 components. Both are formed in the cold state using the slip cast process, differing only in the method in which they are fired **(30)**. NC-435, a fine-grained "siliconized" silicon carbide even stronger than NC-430 **(30)**, is produced by slip casting and offers considerable potential as an economically produced, high strength structural turbine ceramic. The high room temperature strength of NC-435, however, is offset by the gradual strength decrease at temperatures above 1200°C (2192°F) (Fig. III-2) caused by the presence of $\simeq$ 23 volume percent free silicon **(32)**. Tests have shown that silicon metal begins to appear on the surface at temperatures greater than 1350°C (2462°F) **(32)**.

KT SiC is similar to Refel and is produced by the Carborundum Company. It is made up of rather coarse (40 μm) α grains, bonded by secondary β grains and 8-12 vol% free silicon. Unlike Refel, KT SiC contains small amounts of graphite and porosity. Super KT SiC contains a much finer grain structure, consequently its strength is approximately twice that of ordinary KT. Both KT and Super KT are almost exclusively produced by means of extrusion (for furnace radiant tubes) by Carborundum. However, with appropriate production modification they can be formed by other conventional ceramic processing techniques.

As the range of applications for reaction bonded silicon carbide has widened, the demand for a larger range of shapes and sizes has also increased, and cold isostatic pressing has been developed to complement the extrusion process **(33)**. Using this technique it is possible to produce large tubular components (up to 25 cm in diameter (10") and 45.6 cm long (18") and slabs up to 25 cm wide (10") by 2 cm thick (0.8") and 50 cm long (20")) which could not be readily extruded **(33)**. Small, irregularly shaped objects can be mass produced by isopressing. More importantly, irregularly shaped components can be either pressed directly, or pressed and machined in the green condition, so that on firing little or no machining is required **(33)**.

Often, complex shapes can be formed only by injection molding techniques. The use of a thermosetting polymer substituted for the graphite (or carbon) has been proven to be an effective method of injection molding (very similar to transfer molding) of silicon carbide **(34)**. In this process, variables such as polymer volume fraction and SiC particle size distribution play important roles in controlling bake-out shrinkage (2% or less is desirable) Parts formed by this technique, then siliconized have attained 97% theoretical density **(34)**

Recrystallized and reaction bonded SiC are viable candidates for use as high temperature structural materials in an all-ceramic automotive gas turbine engine These materials have demonstrated the ability to withstand thermal fatigue cycling in experimental engines and test rigs Ford has had some success in evaluating reaction bonded SiC (Refel) combustors utilizing a new thin-walled design to minimize thermal stresses **(18)** A reaction bonded silicon carbide stator was evaluated with very encouraging results having been free of cracks after 147 hours at 1054°C (1930°F) **(18)**

Numerous additional programs are under way to develop and fabricate workable stationary components from these materials using available design data.

Reaction bonded SiC, although markedly stronger than recrystallized SiC at low temperatures, falls off in both strength and creep resistance at temperatures greater than 1200°C (2192°F) because of the lower melting second phase present (silicon). A second problem with reaction sintering is that the surface of as-fired components contains substantially more free silicon than the interior of the material **(12)**. Properties of the surface may then be different than those of the bulk material, which may necessitate expensive diamond grinding of the surface to produce a more homogeneous material.

For high temperature stationary parts within a gas turbine engine, reaction bonded silicon carbide should fulfill the material requirements, providing that the geometry of the part satisfies current brittle materials design technology, and that the temperature in the region of application does not exceed 1200°C (2192°F) for extended periods of time.

Where exceptional strength is not critical, stationary parts in service at temperatures up to and above 1370°C (2500°F) may be successfully engineered using a recrystallized form of silicon carbide, since this material does not contain a strength degrading second phase.

Reaction Sintered Silicon Nitride

Reaction sintered (bonded) silicon nitride is formed by pressing (die or isostatically) or molding (injection or slip cast) silicon metal powder, then nitriding the silicon body over a given temperature schedule for times varying from 2-5 days depending on the process and on the size of the components. The final density of RBSN is a function of both the green density achieved in consolidation, and the nitriding schedules. The process is extremely sensitive to both temperature and atmospheric control. Atmosphere in the case of reaction bonded silicon nitride, unlike most ceramic firing processes, is a reactant, and very careful control is required **(35)**. Optimum results have been achieved using a nitriding atmosphere of 96% N_2 containing up to 4% H_2 **(35,36)**. An advantage of the reaction sintering process for producing silicon nitride is the ability to maintain close tolerances of the finished part. Shrinkage due to the elimination of pores is closely matched by the volume expansion on conversion of silicon to silicon nitride such that dimensions of green and fully fired bodies can differ by less than 0.05% **(29)**. This is an important advantage, since finish machining can be reduced considerably. When finish machining is required, this can be accomplished in the partially nitrided state using common carbide-tipped finishing tools **(37)**. If any machining is required after complete nitriding, it must be done with diamond tools.

A second advantage of the reaction sintering process for Si_3N_4 is the ability of the material thus formed to maintain its room temperature strength and maintain good creep resistance through 1400°C (2552°F) (Fig. III-2). As with hot-pressed Si_3N_4, creep resistance can be improved by minimizing impurity content; particularly calcium and aluminum **(38)**. Because of its high porosity (20-30% by volume) room temperature strength is only one-fourth that of hot-pressed Si_3N_4, however strength of RBSN at proposed ceramic turbine inlet temperatures is greater than that of hot-pressed. Room temperature strength can be improved by beginning with very fine silicon particle size (400 mesh = 38 μm = 0.0015"), thoroughly removing oxygen from the nitriding atmosphere, and carefully monitoring the nitriding temperature to prevent melting of unreacted silicon (forming large voids) which can result from the exothermicity of the nitridation reaction **(39)**.

One method of forming reaction sintered silicon nitride is by slip casting. This technique can produce parts with final densities up to 2.7 g cm^{-3}. Shapes produced are limited only to those shapes which can be formed in a plaster negative of the object. Silicon metal powder can be chemically suspended into a castable slip using an alkaline organic as a deflocculant, and water as the polar vehicle **(40)**. The parameters of the silicon metal powder that are considered important are, (1) particle size, (2) particle reactivity, (3) particle size distribution, and (4) particle shape **(40)**. The optimization of these parameters will result in a cast body of high "green" density, resulting in a high final density of the RBSN. Reaction bonded silicon nitride fabricated by this technique has very good mechanical properties. This method can be used for low cost, high volume production of reaction sintered silicon nitride.

Consolidation of silicon powder by die pressing (cold pressing) is expected to be one of the higher volume production techniques used in the manufacture of reaction bonded silicon nitride. Presently, the method is useful for producing relatively straight-walled shapes. Powder can be pressed dry, but more often a temporary binder is used which facilitates densification and imparts added green strength. After nitriding, densities ranging from 2.2 to 2.6 g cm^{-3} can be achieved. Tooling is generally simple and inexpensive.

Cold isostatic pressing is a common method for achieving homogeneously dense silicon powder compacts on parts having a large cross sectional area. Air or hydraulic pressure, applied to an elastomeric bladder, densifies the powder uniformly from all sides. Silicon powder is isopressed either as a billet or to rough shape depending on the required hardware geometry. This preform is green machined to final geometry (if necessary) and the resulting part nitrided to final density (2.3 to 2.7 g cm^{-3}) **(35)** This fabrication method is frequently chosen as the best way to manufacture prototypes which might ultimately be manufactured in volume by a lower cost technique **(35)**.

Injection molding, using a silicon-thermoplastic mixture, is an extremely promising technique for producing complex, highly detailed shapes Typically, densities equal to or higher than those of slip cast or isopressed RBSN (2.1 to 2.7 g cm^{-3} final density) are achieved. Initial costs are comparatively high for injection molding tooling, but when large quantities of close tolerance parts are produced the method is probably the most cost effective fabrication technique currently employed Furthermore, complex shapes produced by this method may, as a second production step, be densified to near theoretical density using hot isostatic pressing (HIP) techniques.

A number of vendors are now supplying reaction bonded silicon nitride by one or more of the fabrication techniques outlined above. As with any ceramic material, properties are highly dependent on fabrication process technology, therefore, it is imperative that these characteristic distinctions be realized not only for RBSN produced by two different vendors, but also for RBSN produced by two or more fabrication processes by a single vendor

The Norton Company produces a reaction bonded silicon nitride, NC-350 produced mainly by cold isostatic pressing of high purity silicon powder followed by nitriding at elevated temperatures to form Si_3N_4 Due to the comparatively low density of NC-350 (only 70 to 80 percent of theoretical) room temperature strength is lower than 100% dense reaction bonded silicon carbide Batch variability in room temperature strength data has been found to correlate directly with density **(32)**. From room temperature to 1200°C (2192°F) a significant strength increase has been observed **(32)** (Fig III-2), however from 1200°C (2192°F) to 1370°C (2500°F) batch to batch variation in samples has resulted in both slight increases and slight decreases in strength. It is believed that variations in impurity levels (oxygen for instance) may account for these strength variations **(32)**. This material may be a strong candidate for low stressed, complex shapes which require good thermal shock resistance.

Another major vendor of reaction bonded silicon nitride is Kawecki-Berylco, the United States licensee for AME (Great Britain) KBI is more versatile than Norton in fabrication technique, routinely producing RBSN by injection molding, slip casting, uniaxially die pressing, and cold isostatic pressing Details of fabrication processes are proprietary, however basic principles are not unlike those previously outlined

As with NC-350, room temperature strength properties are primarily controlled by its ≈ 20% porosity Highest densities may be achieved for KBI material by injection molding (up to 2.7 g cm^{-3}) and by slip casting (up to 2.6 g cm^{-3}) However, the most uniform densities are attained by isopressing of the silicon powder **(41)** High temperature strength properties of KBI RBSN as with NC-350 are very good, due to the minimization of impurities compared to hot pressed Si_3N_4

Si/SiC Composite

The fabrication of silicon silicon carbide ceramic composites consists of infiltrating carbonaceous material with molten Si in a vacuum ($\approx 10^{-2}$ torr) at temperatures ranging from 1450°C to 1600°C (2642°F to 2912°F) and times of the order of 5 min **(42)**. The carbonaceous material can be in the form of fiber tow, fiber cloth, or felt--all of which are commercially available **(42)**. Research on Si SiC composites has been conducted by Fansteel Corporation and Tylan Corporation. However, Silcomp, a material produced by the General Electric Company, has received wide recognition as a viable gas turbine structural ceramic.

The reaction between carbon and liquid silicon forms predominately β-SiC crystallites of sizes in the general range of to 5 µm. The distribution of the starting carbonaceous material is preserved; that is, if the preform consists of a block of uniaxially aligned carbon fibers, the final structure will consist of uniaxially aligned SiC crystallites in a silicon matrix **(43)**. By varying the amount, distribution, and type of carbon in the preform, one can obtain a variety of structures. The flexibility of tailoring the structure as well as the ability to fabricate to final shape (the preform maintains its shape to 0.25% after infiltration provided proper molding procedure is used) are the features which make this material attractive **(43)**.

Silicomp (trademark of the General Electric Co.) is currently produced only in research quantities in two distinct grades; Type TH (high vol% silicon carbide) and Type F (low vol% silicon carbide) and a number of intermediate grades; one of which is [illegible] below: **(42)**

Designation	**Vol% SiC**	**R. T. Bend Strength (MN/m², ksi)**	**R. T. Elastic Modulus (MN/m², psi)**	**Density (g/cm³)**
Type TH	80-85	483, 70	3.93×10^5 57×10^6	2.87
Type THL	40-45	331, 48	3.03×10^5 44×10^6	2.70
Type F	20-25	207, 30	2.00×10^5 29×10^6	2.60

Strength of Silicomp™ is primarily dependent on the SiC content: higher volume of SiC leads to higher strength. In common with other silicon-containing ceramics, such as reaction bonded silicon carbide, the strength decreases abruptly at the melting point of silicon but then remains nearly constant to 1600°C (2912°F). Due to the fibrous SiC microstructure, strength never decreases to zero as the Si melting point is exceeded **(44)**. Present measurements indicate that very little strength degradation occurs with time in Si/SiC **(45)**. Also, large cracks that form as a result of fracture above the melting point of Si can be healed by molten Si, resulting in a recovery of the original strength below the melting point of Si **(45)**.

Because Types TH and THL are made from a carbon filament tow as a starting material, these types have anisotropic properties (strength, elastic modulus) because of the aligned nature of the SiC phase, i.e., the transverse properties of uniaxially aligned Si/SiC composites are primarily governed by the matrix Si, and the longitudinal properties by the SiC filament **(42,43,46)**. Type F Silcomp™ is made from a carbon felt and has, therefore, isotropic properties **(42)**.

To date, several turbine component parts using Si/SiC have been fabricated and tested in machinery or simulators **(44)**. As technology develops for this relatively new material, properties of fabricated parts should improve. Precision casting within a mold is now used to make Si/SiC components to shape **(47)** with only minimal machining required, contributing to the low cost with which complex parts may be produced. For complex structural components subjected to moderate stresses and temperatures of up to 1200°C (2192°F), Si/SiC composites offer considerable potential.

SIAlON

SiAlON a new class of material based on the β-Si_3N_4 structure was first proposed in 1972 through independent studies by Jack and Wilson in England and Oyama and Kamigaito **(49)** in Japan. Substitutions are made within the basic β-Si_3N_4 unit cell of aluminum for silicon, simultaneously with oxygen for nitrogen. Its formula can by represented by $Si_{6-x}Al_xN_{8-x}O_x$, where "x" represents the number of nitrogen atoms replaced by oxygen atoms, ranging from 0 (pure β-Si_3N_4) to 4.2 **(50)**. Although originally believed to be a solid solution between Si_3N_4 and Al_2O_3, more recent work **(50)** has shown SiAlON to be a solid solution of β-Si_3N_4 and AlN-Al_2O_3. A second crystalline phase labeled by Jack **(48)** as the x-phase, is now thought to be represented by the formula Si_3N_4 $6Al_2O_3$ $3SiO_2$ **(51)**.

Starting powders to produce SiAlON usually include Si_3N_4, Al_2O_3, AlN, and sometimes SiO_2 in molar ratios necessary to give the particular composition desired. To attain the highest density possible by reaction sintering, powders are usually ballmilled for long times **(52)**. Densification is also enhanced by reducing Si_3N_4 content (thus increasing Al_2O_3 content) of the starting mixture **(52)**. SiAlON, thus produced, is usually characterized not only by higher density, but also by high x-phase microstructures, formed if the composition contains excess oxygen **(50)**. Lange **(53)** observed that the microstructure of such samples suggested that the presence of liquid during sintering is an important factor in achieving high density. The effect of the x-phase on thermal expansion properties of SiAlON is small, and for practical purposes can be ignored. Low porosity (consequently high x-phase) levels are essential if its strength, impact resistance, and thermal shock resistance are to be maximized.

However x-phase is shown to have a detrimental effect on fracture toughness **(54)**. Opinions differ among SiAlON experts as to which is more desirable, single phase SiAlON (R.R. Wills 54), or multi-phase SiAlON (Jack 48), and the debate shows no sign of resolution.

SiAlON may be prepared by hot-pressing, the operation being somewhat easier than with silicon nitride because of its inherent ease of densification, and because of its extreme chemical stability at hot-pressing temperature, the purer SiAlON does not form the surface carbide layer which is common on as-pressed silicon nitride **(55)**. Fully dense bodies can be obtained at temperatures as low as 1500°C (2732°F) at 27.6 MN m^2 (4000 psi) for two hours with no x-phase detectable and at 1700°C (3092°F) at 27 6 MN m^2 (4000 psi) without a holding time **(56)**.

SiAlON materials can also be reaction sintered in nitriding atmospheres to approximately 97% of theoretical density after forming by conventional

THERMAL EXPANSION OF CANDIDATE HIGH TEMPERATURE CERAMIC MATERIALS

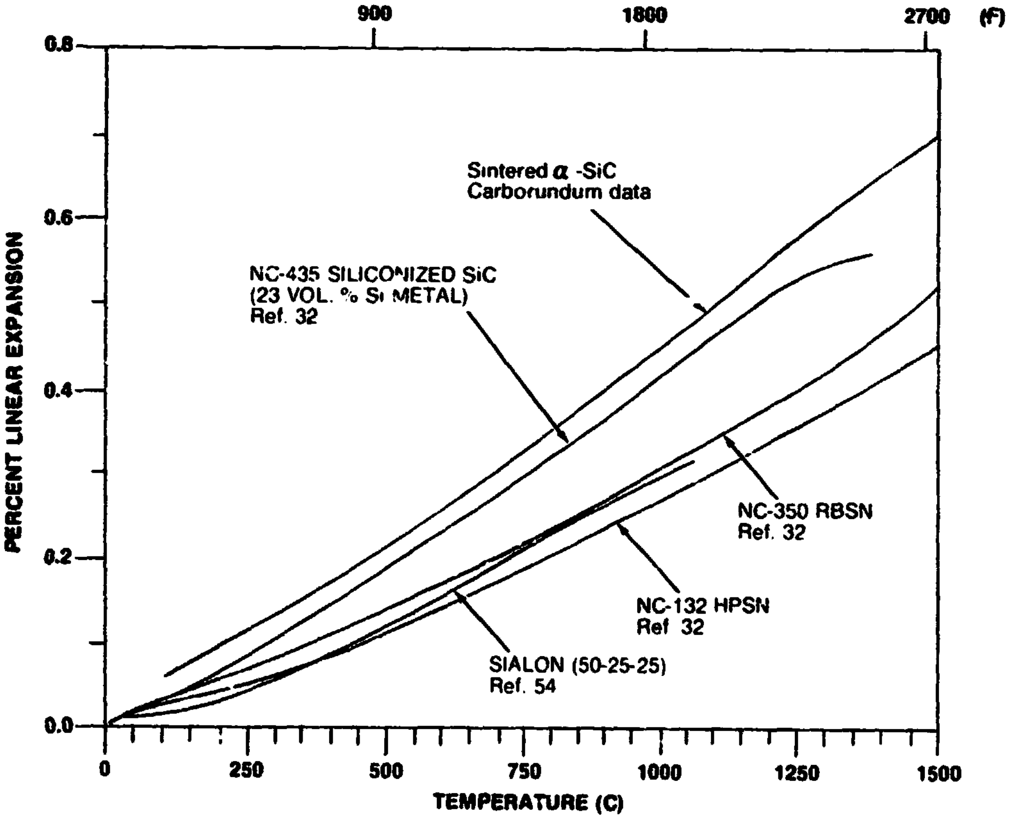


Figure III - 3

means, e.g., die pressing, slip casting, isopressing, injection molding, or extrusion and exhibit moderate, controllable shrinkage on sintering. Impurities have been found to be responsible **(56)** for the sintering ease of SiAlON proclaimed **(57)** during its very early stages of development, thus a more desirable (containing fewer impurities) SiAlON is not so easily sintered **(56)**. At this time, the (pressureless) sinterability of SiAlON with or without additives is really no better than the sinterability of silicon carbide or silicon nitride.

There are certain dangers in making comparisons between more highly developed commercial materials and an essentially new material, since microstructural changes in the reaction-sintered SiAlON may be brought about at a later date by the use of different starting powders and/or processing schedules **(58)**. It is possible to state that for all practical purposes the thermal expansion coefficients of SiAlON can be considered identical to both hot pressed and reaction-sintered Si_3N_4 **(58)** (Fig. III-3), and that strength properties of present day reaction sintered SiAlON is similar in magnitude to siliconized silicon carbide materials, decreasing sharply in strength above 1200°C (2192°F) not because of free silicon melting, but because of subcritical crack growth caused by a viscous grain boundary phase **(52,53)**. This sharp strength decrease may be at least partially alleviated by decreasing impurity content (particularly Ca) in the starting powders **(52)**.

SiAlON can best be described as a lower porosity reaction-bonded Si_3N_4 since its fracture toughness, fracture surface energy, and thermal conductivity are nearer those of reaction-bonded rather than hot-pressed Si_3N_4 **(58)**. The strength of SiAlON is likely to be higher than that of reaction-bonded Si_3N_4, but its thermal shock resistance equivalent, the advantage of higher strength being counteracted by a much lower thermal conductivity **(58)**.

SiAlON offers the potential for pressureless sintering to full density, for good fabrication capability, and for developing high strength. High temperature oxidation resistance may be good because the aluminum in the structure may form an Al_2O_3 protective layer, although little research has been done in this area. SiAlON may not be the most suitable material for areas where good thermal shock resistance is important because of its low thermal conductivity. However, SiAlON may offer good potential for high temperature structural insulators. Thermal properties, and all other properties are directly related to the phase equilbria of the system, an enormous area of crystallography which is as yet unresolved among researchers. SiAlONs' phase equilibria may turn out to be an asset, since depending on the application either a single phase or multiphase microstructure may be specified—ideally a microstructure incorporating, but not sacrificing the best qualities of each phase. SiAlON materials are presently at an infant stage of development; there remains a tremendous amount of basic research to be done before they can be considered exploitable for use in all-ceramic gas turbine engine.

Low Stress Parts

Several parts in an all-ceramic gas turbine engine will not be subject to significant levels of stress. In these cases, where strength is not an important factor, the use of certain specific ceramic materials, rather than metals, may offer greater advantage.

Glass-ceramics have been used as regenerative heat exchangers in gas turbine engines since 1965, initial development being pursued by the Ford Motor Company **(59)**. Several suppliers are also actively involved in research and development of ceramic regenerators, e.g. Corning Glass Works, Coors Porcelain Company, GTE Sylvania, NGK Insulators, W.R. Grace Company, Owens-Illinois, and the General Electric Company. Presently, the ceramic regenerator is the most well-established demonstration of ceramic practicality in a gas turbine engine.

The major materials requirements for a glass-ceramic regenerator are low thermal expansion up to 1000°C (1832°F), long-time dimensional stability and phase stability up to 1000°C (1832°F), corrosion resistance with respect to sulfuric acid and sodium salts, and the ability to operate at least for short times up to 1100°C (2012°F) **(60)**. The glass-ceramics LAS, MAS, MAS/LAS, and AS meet these requirements best. In addition to these four groups, proprietary materials are being developed by the Ford Motor Company which may either be modifications of these existing systems or entirely new chemical systems

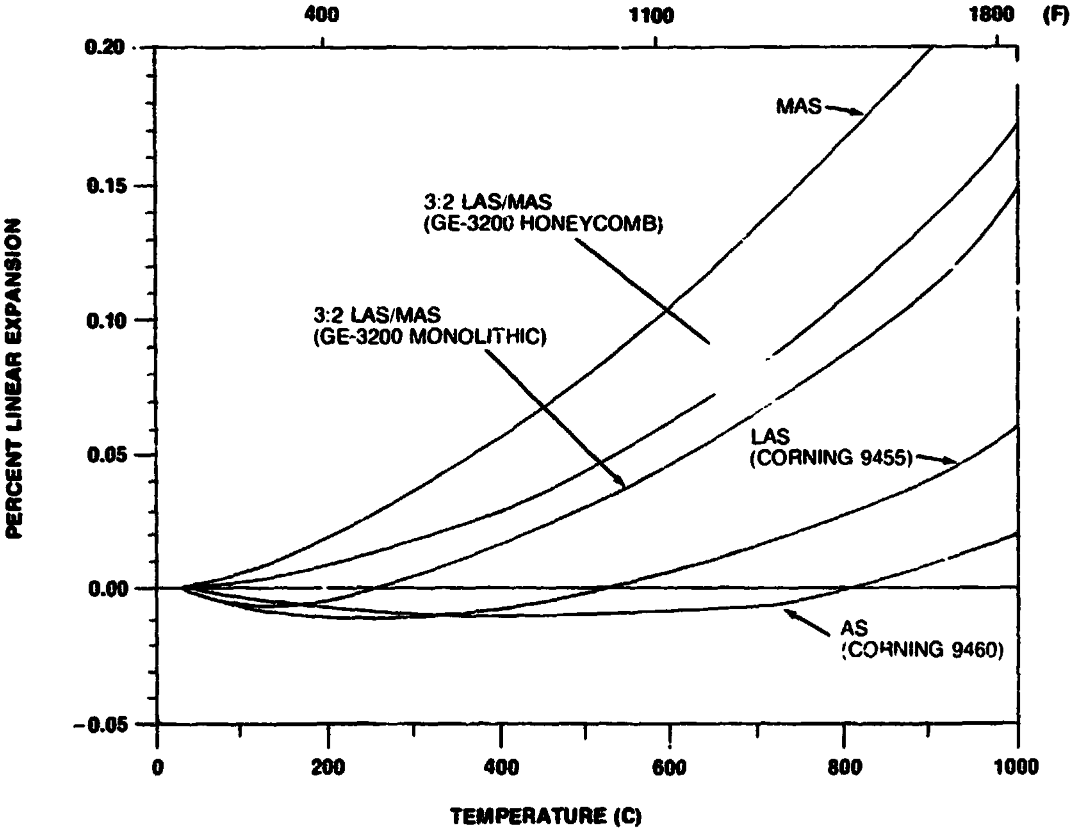
Lithium Alumino-Silicate (LAS)

LAS materials, based on the β -spodumene crystal structure, were first to be developed, consequently they have received the greatest attention as heat exchangers. They possess excellent thermal shock resistance resulting from a near-zero expansion coefficient (Fig. III-4) and excellent mechanical properties which result from glass-ceramic processing methods. However, chemical instability of LAS materials was observed during long-term testing in the turbine exhaust environment related to attack by sulfuric acid and sodium **(60)**. Sulfuric acid, formed in the products of combustion of sulfur-containing fuel, condenses on the cold side of the regenerator and attacks that face. This chemical attack (exchange of Li^+ for H^+) progresses to the point where cracks are formed due to volume change, and core break-up occurs. Sodium, which enters the engine through ingestion of road salt, salt water, or from contaminated fuel, chemically attacks the hot side of the regenerator (Na^+ for Li^+) and causes a deterioration of the LAS ceramic **(61)**. Because of its high susceptibility to chemical attack, LAS glass-ceramics are no longer considered as candidate regenerator materials for gas turbine use.

Magnesium Alumino-Silicate (MAS)

MAS materials, based on the α -cordierite crystal structure have proven to be essentially impervious to chemical attack and have demonstrated their potential as regenerator core materials in engine durability testing at 800°C (1472°F) **(61)**. A major problem with MAS ceramics, however, is their higher thermal expansion when compared to LAS (Fig III-4). At temperatures greater than 900°C (1652°F), thermal stresses generated by the higher expansion coefficient can cause matrix cracking. Different MAS formulations have been found to vary sharply (particularly among various manufacturers)

THERMA NSION OF CANDIDATE REGENERATOR MATERIALS



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in their stability to temperatures of 1000°C (1832°F) **(62)**. At the onset of the MAS developmental program, researchers were optimistic toward the possibility of producing a lower expansion MAS material. This goal has been found to be more difficult to achieve than originally expected. The availability of a low-expansion MAS material depends upon the progress made by the various ceramic companies in fabricating and firing a full size regenerator of this material. If attainable, MAS ceramics would probably be the most desirable regenerator core materials because of their good strength properties, extreme chemical stability, and also because of the excellent economic potential afforded by this material (MAS raw materials are relatively abundant and inexpensive.)

MAS/LAS

Data obtained by researchers at the General Electric Space Sciences Laboratory indicate that combinations of MAS and LAS materials, processed by conventional fabricating techniques, have good corrosion resistance and lower expansion characteristics than MAS alone **(60)**. X-ray diffraction examination of these MAS/LAS combinations reveal the presence of both -spodumene (LAS) and α-cordierite (MAS) in bodies produced by conventional glass-ceramic processing and heat treatment. Most of these MAS/LAS combinations contain MAS as the predominant phase, usually in a 3:2 ratio by weight. The corrosion resistance of such bodies appears to be almost equal to MAS alone thus suggesting that MAS-LAS materials may offer potential for use in gas turbine heat exchanger applications **(60)**. Present problems in research relate to the need for additional chemical analysis in determining the role of Li_2O and its distribution within specimens to ensure that the fired material retains sufficient Li_2O to provide the desirable low-expansion behavior **(60)** Research and development on MAS/LAS glass ceramics may eventually lead to a marketable product combining the best properties of LAS and MAS while simultaneously minimizing the shortcomings of each

Aluminum - Silicate (AS)

AS, alternately referred to as "leached LAS" or "aluminous keatite", is basically an LAS regenerator matrix from which all the lithium oxide (Li_2O) has been removed by an additional processing step (usually by leaching with hot H_2SO_4). This acid-leaching of the lithium ions causes microcleavage openings within the basic β-spodumene crystal structure. After exchange, it is possible to adjust the material's thermal expansion by firing in excess of 1000°C (1832°F), which partially collapses the microcleavage openings and introduces some mullite ($3Al_2O_3$-$2SiO_2$) depositions at the grain boundaries, thereby inhibiting grain growth **(63)**.

The effect of the microcleavage openings in the aluminous keatite material is manifested in a reduction of about 40% in modulus of rupture values vs. standard LAS material. However, an even larger 60% reduction in elastic modulus produces a substantially higher strain tolerance. The aluminous keatite acts more spongy; this factor, combined with the extremely low thermal expansion coefficient tailored in by the firing schedule, yields a material with a much higher thermal stress safety factor than the parent LAS material **(63)**.

Chemical stability of AS materials is comparable to that of MAS; the material is virtually unaffected in high sodium or sulfuric acid environments. Thus, thermal-stress resistant aluminum silicate regenerator materials are extremely promising candidates for use in gas turbines subject to road salt or marine environments, or with sulfur-bearing hydrocarbon fuels, such as diesel oil.

A detailed account of raw material preparation and regenerator core matrix fabrication of glass ceramics is beyond the scope of this paper, however, excellent descriptions of these various processes can be found in Reference 62. Typically, four basic fabrication techniques are employed for making ceramic cellular structures **(62)**:

The coated paper process - *Low ash paper is run through a ceramic slurry, dried, crimped, then wrapped around a reel to form the regenerator matrix. This method can yield matrices with sheet thicknesses as low as 0.0076 cm (3 mils) with uniform cell geometry and good joint bonds.*

Extrusion - *The simplest of the fabrication methods yielding the most uniform wall thicknesses and cell structures. Some problems involve simultaneously obtaining thin walls and large pieces, and the uncertainty of die wear costs.*

Embossing and Calendering - *Quite similar processes, advantages being a highspeed single sheet operation with no paper carrier and the rectangular cell opening. The capability of making a sheet that is less than 0.013 to 0.015 cm (5 to 6 mils) thick with either of these processes has yet to be demonstrated. The art of calendering or embossing ribbed tape containing ceramic powder is still in its infancy, and technological progress is continuing at a rapid pace.*

Cost considerations and engineering factors must be considered in selecting a fabrication process. Uniformity of wall thickness and cell structure, wall porosity and joint bonding are important factors from a thermal shock, performance and mechanical property standpoint **(62)**.

General Low-Stress Ceramics

It is conceivable that in certain gas turbine engine exterior structural applications such as housings and cover plates, the advantages of ceramics may outweigh, point-for-point, those of metals, the end result being a more efficient and economical vehicular powerplant. Perhaps the greatest advantage stems from the comparatively low bulk density of ceramics; most are less than 40% of the weight of traditional ferrous castings. Although ceramics will probably never be comparable to ferrous castings on a price per pound basis, if produced in volume quantities they do offer the potential for direct competition with aluminium alloys. Since vehicle weight savings is now, and will continue to be of prime importance, the choice will probably be an economic one between ceramic materials and aluminum alloys. It is expected that three-dimensional stress analysis techniques, and newly developing methods for joining ceramics to ceramics and ceramics to metals will serve to minimize the problem of inherent ceramic brittleness.

An important application for low stressed ceramics is in the field of insulators. Materials with low thermal conductivity and low thermal expansion will be needed to shield or isolate metal structural parts from the intense heat of the hot flow path. Many of these materials will probably be alumina-silica or alumina-fiber based.

Even though these structural applications do not require ceramic material(s) with exceptional strength properties, it would be absurd to expect that a medium or high strength ceramic would be rejected, especially if it displayed fabrication potential for large, contoured parts (probably formed by slip casting), and, more importantly, demonstrated an economically feasible process for manufacturing such parts. Sinterable materials, such as Carborundum's α -SiC or GTE Sylvania's sinterable Si_3N_4 are among the most promising candidates, demonstrating a greater potential for low cost fabrication of complex shapes than any other Si-C or Si-N based ceramic, with the added bonus of medium to high strength properties Glass-ceramics are not strong enough, and recrystallized SiC is marginal in strength. Reaction sintered silicon carbide and silicon nitride are more expensive, pound-for-pound, and not as strong as the sintered materials. Ultimately, the material with the lowest cost fabrication technique will win out for this structural application, be it metal or ceramic.

Ceramic Processing Requirements

Coatings for oxidation/corrosion protection

Silicon Carbide

Because fine powders of silicon carbide can be, and typically are densified (by hot pressing or by pressureless sintering) at temperatures greater than 2000°C (3632°F) without dissociation of the basic Si-C structure, only a minuscule amount of sintering additive is necessary, i.e., if the sintering temperature can be increased, the amount of sintering additive may be lessened. As the amount of sintering aid is decreased, it becomes less likely for such impurities to react with oxygen and form glassy, strength-degrading secondary phases The use of high-purity α -SiC powder in making Carborundum sintered α -SiC is an important reason for the exceptionally high resistance to oxidation of the product **(64)**. General Electric sintered β -SiC forms a very thin, coherent, protective film of SiO_2 under oxidizing conditions and is essentially inert in H_2, H_2S and high-purity N_2 at high temperatures **(65)** Thus, coatings to protect against oxidation are unnecessary for sinterable SiC Hot pressed SiC, however, does display a marked improvement in high temperature oxidation resistance if a layer of CVD SiC is applied to the surface **(66)**. This is probably due to the high purity of the CVD material in contrast to the hot pressed material which contains excess impurities added as sintering aids **(6)**.

In the oxidizing atmosphere of the gas turbine engine, both sintered and hot pressed SiC show remarkable resistance to corrosive degradation, even at turbine inlet temperatures of 1370°C (2500°F) and in atmospheres heavily contaminated with Na, V, and S **(65)**.

Silicon Nitride

As previously reported (see "Sinterable Silicon Nitride"), thermal decompostion becomes significant for Si_3N_4 at temperatures greater than 1700°C (3100°F), thus complete densification at higher temperatures necessitates the use of pressure, inert atmospheres, and sintering additives. During oxidation at high temperatures, diffusion of the sintering additives to the surface causes the formation of a strength-degrading silicate glass ($MgSiO_3$ if MgO is the sintering additive) which is reactive to the substrate Si_3N_4. Other sintering aids, i.e., zirconia and yttria compounds, form more refractory glasses which are somewhat less reactive with the substrate Si_3N_4

In an attempt to eliminate or reduce the degradation in strength normally associated with oxidation of hot pressed Si_3N_4, a surface coating program was initiated by the Ford Motor Company **(36)**. From this study it was found that all coatings evaluated, with the exception of CVD Si_3N_4, showed severe spalling of the surface which could be seen with the unaided eye. A significant difference in thermal expansion coefficients between the chemical vapor deposited coatings and the substrate NC-132 was believed to be the reason for failure of these coatings. Pure CVD Si_3N_4 possesses extremely high oxidation resistance due to the formation of pure SiO_2 on the surface, and a compatible thermal expansion coefficient with the substrate Si_3N_4. Further work is expected from other researchers on improving the application of CVD Si_3N_4 to a substrate, and in evaluating the benefits of such a process.

Joining of Ceramics

Whenever ceramics will be used in a gas turbine engine, engineers will have to face the challenge of joining both ceramics to ceramics and ceramics to metals. Joints in ceramic systems may be treated as both problems and opportunities **(67)**. Problems arise because load transfer between nonplastic members leads to high stress concentrations; opportunities exist, however, since joints in ceramics provide a means to interrupt the continuity of a structure, thereby limiting thermal strains and stresses in much the same way as do expansion strips in concrete highways.

Joints must perform two major functions (in addition to holding the parts together). First, they must be able to take up contact stresses resulting from the assembly of imperfectly matched components. Secondly, they must attenuate the stresses resulting from differential thermal expansions of different components **(67)**. Typically, a compliant layer material is used in the joint which has some degree of plasticity to flow under Hertzian, frictional, and thermal stresses, but not so much that it can be squeezed completely out of contact with components being joined.

The soundness of ceramic to ceramic and ceramic to metal joints and seals must be assured to guarantee the performance of the structure in which they are incorporated. Joint evaluation tests fall into the following categories: mechanical tests (tensile, flexural, peel, shear strength, etc.), electrical tests, leak tests, thermal tests (thermal conductivity, thermal shock, and thermal cycling), vibration and mechanical shock tests, corrosion tests, oxidation tests at high temperatures, and other, more specialized tests. In addition to these standardized tests, there is a pressing need to evaluate the overall quality of the bond area nondestructively. Techniques such as X-ray and ultrasonic inspection offer promise but still are not as versatile for industrial usage as would be desired **(68)**.

Ceramic to metal and ceramic to ceramic joining methods fall into five broad categories: a) adhesives, b) mechanical connections, c) fusion joining, d) solid-phase joining and e) liquid-solid phase joining.

Adhesives

There are numerous organic and inorganic adhesives and sealants to make effective ceramic to ceramic and ceramic to metal joints. Such adhesives fall into two general categories — polymers and inorganic ceramics.

Silicone rubber polymers have skeletons composed of Si-O-Si-O with organic groups attached to it. Most silicone adhesives are one-component room temperature vulcanizing (RTV) that cure when exposed to moisture in the air. Supplied ready-to-use, the material cures to a tough, rubbery solid which remains flexible from −65 to 260°C (−85 to 500°F). The material absorbs shock, vibration, resists weathering, ultraviolet light ozone, most oils and chemicals, and shrinkage. Fully cured silicone rubber displays a tensile strength of 2.07 MN/m^2 (300 psi) at room temperature and can be used for extended periods of time at temperatures up to 175°C (350°F). For shorter periods of time RTV silicones withstand temperatures as high as 260°C (500°F) **(69)**. Because of the low strength of silicone rubber bonds, the material is probably better classified as a sealant, rather than as an adhesive. It may find application as a stress-relieving gasketing material between mechanically joined ceramic-metal and ceramic-ceramic parts in a gas turbine engine.

Epoxy resins have exceptional mechanical strength, most of which is maintained under conditions of moisture and high humidity. Most widely used of the epoxies are the bisphenol A type, which provides excellent electrical and mechanical properties, heat resistance, dimensional stability and adhesion to most materials. Gaining in use are the cycloaliphatic epoxies, which offer good weatherability and arc tracking resistance in addition to the properties of the bisphenol A group A third type of epoxy resin - the epoxidized novalacs - have even better heat resistance and higher reactivity with hardeners. Strength of all types can be increased when the resins are compounded with reinforcing fibers of glass or minerals. Tensile strengths range from 28-140 MN/m^2 (4,000-20,000 psi) depending on the resin and filler material employed. One-part epoxy systems require heat for curing; two-part systems usually cure at room temperature. Properties of both types are better when heat-cured, however. Most epoxies can withstand temperatures of 120°-150°C (250°-300°F) for long periods of time. Some one-part epoxies can survive 200°C (400°F) continual service and still retain a significant percentage of their mechanical properties. Except for short term service, epoxies should not be used above 230°-260°C (450°-500°F) **(70)**.

Although costly, polyimides are a family of some of the most heat and fire resistant polymers known. Such adhesives generally contain aluminum powder to provide the thermal expansion characteristics of metal substrates and to improve heat dissipation. Polyimide adhesives can operate continuously in air at 260°C (500°F); service temperature for intermittent exposure can range from cryogenic regions to as high as 480°C (900°F) at which temperature it still retains 31 MN/M^2 (4500 psi) tensile strength. Polyimide adhesives maintain useful properties for over 12,000 hr. at 260°C (500°F), 9,000 hr. at 300°C (575°F), 500 hr. at 345°C (650°F), and 100 hr. at 370°C (700°F) **(71)**.

For high temperature bonding up to 1705°C (3100°F) inorganic adhesive cements (ceramic cements) must be used. These are available in two basic types: air drying cements and chemical-set cements. Air drying cements cure through loss of moisture (or solvent) by evaporation. Chemical-set cements cure via an internal chemical reaction which does not require exposure to air. Chemical-set cements can be divided into two classes, the exothermic, which give off heat in setting; and the non-exothermic, which do not create h[illegible] the chemical setting action. There are numero[illegible]s of ceramic cements, however most are alumino-silicate based, most resist temperatures up to at least 1093°C (2000°F) and most are resistant to acids (except hydrofluoric) **(72)**. Strengths of ceramic-bonded joints are usually not very high, being similar in magnitude to RTV silicon rubber. Both tensile strength and shear strength of the ceramic bond are always below 6.9 MN/m^2 (1000 psi), which compels the designer to incorporate ceramic adhesive bonding and mechanical bonding only for the lowest-stress application

Mechanical Bonding

The first rule in designing mechanical connections is to design joints in which loads are distributed uniformly and the ceramic is kept in compression This is particularly important wherever large parts are joined. Examples of mechanical joints are shown in Fig III-5 Designs requiring drilling of the ceramic and ground or rough-cut edges should be avoided. Gasket seals should be rigid with bolts torqued evenly to the specified values. When gaskets are required, these should yield sufficiently to equalize loads but not be subject to cold flow. Gasketing material depends on temperature, loading, chemical environment and degree of required hermeticity. Gaskets are necessary if:

- joints must be fluid tight
- the unit loading anywhere on the ceramic part exceeds 10% of its failure stress (in that mode of loading)
- vibration is expected
- notable temperature variations are foreseen **(73)**

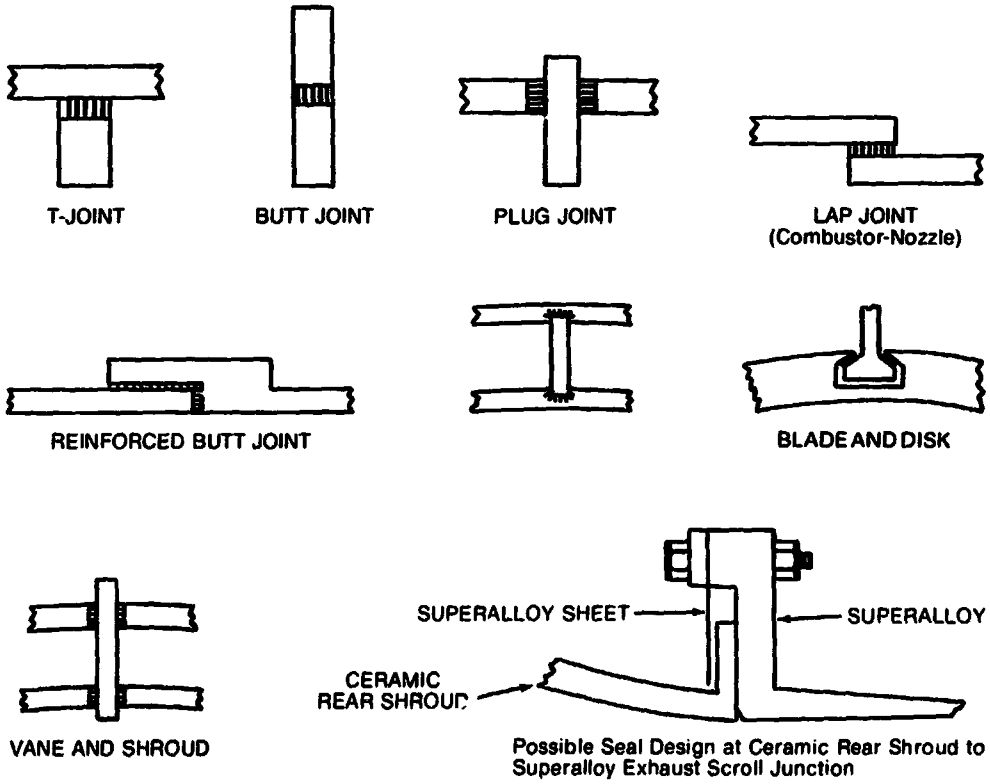
Pure platinum has been used as a stress-relieving cushion between turbine blades and disks, but for such an application its flow stress may be so low that it may be squeezed out of the joint completely **(67)**. The use of superalloys has been found to be more successful for such an application.

Fusion Joining

In fusion joining, the base materials are heated until they melt and fuse. The heat required for fusion can be produced by an electric arc, an electron or photon beam, or the resistance of the base materials to an electric current. This category includes the numerous arc-welding and resistance-welding processes. There appears to be little application of fusion joining in producing ceramic-to-metal seals, since most ceramic materials cannot withstand the thermal shock associated with welding. Limited success has been achieved, however, with electron beam welding of ceramic-to-metal joints **(68)**.

TYPICAL CERAMIC/CERAMIC AND CERAMIC/METAL JOINT CONFIGURATIONS

(AFTER REF. 67)



Possible Seal Design at Ceramic Rear Shroud to Superalloy Exhaust Scroll Junction

Figure III - 5

Solid-Phase Joining

All processes in this category accomplish bonding without changing the solid state of the joint's materials. While most of the processes require heat, the materials in the joint do not become molten. Pressure is usually required to effect joining. Several of the solid state joining processes have been used successfully to produce ceramic-to-metal seals. Among them are the following: diffusion welding (or bonding), pressure welding, gas pressure bonding, and ultrasonic welding. Electroforming or electrodeposition welding, and high energy welding are also included **(68)**.

Liquid-Solid Phase Joining

This category includes soldering and brazing—the processes most widely used in fabricating ceramic-to-metal seals. The American Welding Society includes an arbitrary temperature restriction in defining the processes, soldering is done at temperatures below 427°C (800°F) and brazing is done at temperatures above 427°C (800°F) **(68)**. Generally, soldering is done with metallized glass parts and brazing reserved for crystalline ceramic parts. The joint assembly is heated to a temperature below the melting temperature of either of the base materials but above the melting temperature of the filler metal, thus a liquid is formed at the interface between the two solid members, and the molten filler metal is distributed throughout the joint by capillary attraction. Joining is accomplished when the filler metal solidifies **(68)**.

Because most filler metals do not readily wet ceramic surfaces, metallizing procedures have been developed to overcome this difficulty. Glass surfaces (most often joined by soldering) may be metallized by the following techniques:

Sintered Metal Powder Processes - *Finely divided metal powders (molybdenum, tungsten, rhenium, iron, nickel or chromium) plus a suitable binder to form a suspension are painted onto the surface to be metallized. Then the coating is sintered to the ceramic at temperatures of 1250°C (2282°F) or above. Certain metal oxides may also be added to the fine metal powders as a means of improving adhesion.*

Reactive- or Refractory-Metal Salt Coating - *After painting onto, or immersing the ceramic in a solution of a refractory metal salt, the ceramic is dried and heated to reduce the metal salt, leaving a thin, adherent metal coating on the surface of the ceramic.*

Vapor-Deposited Coating - *These methods of metallizing fall into two general categories; chemical vapor deposition and physical vapor deposition. In CVD metallizing, the coating vapors chemically react with the material being coated, whereas in PVD the material composing the coating is identical with the source material.*

Electroplating - *Nickel, copper or other metals can be deposited on ceramic using conventional ceramic electroplating methods, or, in some cases, the coatings are prepared by electrically reducing oxides of the desired metal. The metals used in ceramic to metal joints are also frequently plated.*

After metallizing, glass may be joined using solders based most often on indium or on the tin-lead system. Eutectic 63 tin - 37 lead begins to melt at 182°C (361°F) **(68)**.

Brazing of crystalline ceramics is a much more critical operation than soldering of glass; extensive knowledge is necessary to select the proper process, filler metal, atmosphere and brazing cycle. Instead of low melting metals and alloys as used in soldering, brazing filler metals are based on the noble metals, the heat resistant metals such as nickel and cobalt, certain reactive metals such as titanium, beryllium, and zirconium, and the refractory metals **(68)**.

Since brazing is conducted at high temperatures, the major bonding mechanisms (between conventionally metallized ceramics and the metal parts to be joined) are reactions between the base metals and filler metal, diffusion of the base metal and filler metal constituents across the joint interface, and the formation of intermetallic compounds **(68)**.

One of the most widely accepted metallizing techniques used for high temperature ceramics is known as the "moly-manganese" process. In this process a slurry consisting of powdered molybdenum and manganese, with additions of iron, silicon, titanium oxide, calcium oxide, and organic binders is applied by spraying, painting or silk screening. The ceramic-to-metal joint is then heated to 1350°-1600°C (2462°-2912°F) in a wet hydrogen atmosphere or in a vacuum to effect joining. At these temperatures, the oxides form a eutectic melt that reacts with the ceramic and the oxide on the metal, as well as the sintered molybdenum and manganese, to form a bond **(73)**. Tensile strengths of 196 MN/m^2 (28,400 psi) have been reported for a 94% alumina ceramic metal joint using the moly-manganese joining method **(68)**.

Another process for joining high temperature ceramics is the "active metal" process. The ceramic and metal parts are coated with a slurry of titanium or zirconium hydride in nitrocellulose, and then joined by heating to 1650°C (3002°F) in vacuum This decomposes the hydride and releases the free metal for bonding. Joining depends on the ability of titanium or zirconium metal to adhere to oxide surfaces without the need for fluxing. Bond strengths are slightly lower using the active metal process vs the moly-manganese process **(73)**.

Also grouped within the heading of liquid-solid phase joining may be the method of flame spraying silicon into the joint area between components which are to be joined, then reaction nitriding the joint to form reaction bonded silicon nitride. This method has not been extensively employed in joining of ceramics as yet, however it is a method of producing a stable, high temperature joint with strengths upwards of 138 MN/m^2 (20,000 psi) at the interface. Presumably, this joining method will become more attractive when a method for completely nitriding the silicon while flame spraying is perfected As yet, complete nitridation of the silicon while flame spraying with a nitrogen-containing carrier gas has not been successfully demonstrated.

Slip cast bonding can be used successfully to bond reaction sintered silicon nitride units into a homogeneous bond. A low viscosity, chemically suspended silicon slurry is introduced into a casting volume which is defined by the walls of the porous presintered silicon components. The slurry solidifies by extraction of the vehicle through the porous silicon structures by capillary action, producing a coherent mass of silicon within the casting volume which when nitrided results in a homogeneous silicon nitride body. The joining volume is generally small; therefore, to avoid gas entrapment and premature bridging the bonding slip must have high fluidity. In addition, the slip must completely wet the surfaces of the structures to be joined, the density of the bond must be readily controllable, and the green shrinkage (i.e., shrinkage after the bonding material is thoroughly dried) must be low to prevent bond "pull away" or bond checking. Using slip cast bonding, the inverted channel stator and the tridensity rotor have been successfully manufactured **(75)**.

Fabrication techniques have also been developed which enable a contoured hub to be simultaneously hot pressed to theoretical density and bonded to a reaction sintered blade ring to form an integral, duodensity turbine rotor. Using this technique, the bond between a reaction sintered blade ring and hot pressed hub in a turbine rotor assembly can be made as strong as the weaker of the two parent materials **(75)**.

Machining Methods

The machining of ceramic components is a critical step from both economic and technological standpoints. It is important economically because it often represents the major cost of producing a ceramic component. The technical importance of ceramic machining results from the fact that it affects or controls much of a ceramic's behavior, e g . optical, magnetic, and piezoelectric performance. However, of greatest importance in general, and to structural ceramics in particular, is the effect of machining on strength and fracture behavior **(76)** Those machining methods with greatest significance (or greatest potential significance) for ceramics include diamond machining, electrical discharge machining, electrochemical machining, and ultrasonic abrasive machining

Diamond Machining

This has traditionally been the predominant means of shaping, i.e , cutting or grinding, very hard ceramics such as silicon carbide or silicon nitride Although much information is available from ceramic material researchers and suppliers, and specialty machine shops relating wheel grit sizes, down feeds, and surface speeds to cutting grinding efficiency **(18,77)**, only recently has serious attention been given to the effect of diamond machining on the mechanical or physical properties of ceramics. Grinding processes that leave directional grooves or striations can lead to strength effects related to the direction of machining. It has been shown that strengths with tensile stresses normal to the machining grooves or striations can be substantially lower than those with tensile stresses parallel to the machining striations **(76)**. These grinding-direction effects generally become more important with decreasing grain size.

It has been shown **(75)** that flexural strength of relatively large-grained ($>10\mu m$) polycrystalline ceramics can be substantially improved (50 to 200 percent for large MgO and CaO crystals) by diamond grinding at high removal rates. This strengthening is due primarily to the extensive depth of workhardening which induces compressive stresses in the surface and limits slip-induced crack nucleation **(76)**.

Such is not the case with higher strength, fine-grained ($< 10\ \mu m$) ceramics, where flaws induced by machining cover several grains and often limit or negate the benefits of surface compressive stresses. Machining can often weaken fine-grained, high-density materials where strength becomes highly dependent on surface defects. In order to utilize the maximum potential strength of such materials, grinding at very low removal rates must be followed by diamond lapping of the surface, which is costly and time consuming.

For all practical purposes, diamond machining is limited to relatively simple operations (i.e., making straight cuts, grinding flat surfaces, or drilling round holes). Attempts to develop diamond machining techniques which could be used to grind a small one piece gas turbine rotor out of a fully densified silicon nitride blank met with little success in a study done by the Norton Company **(78)**. Metal bonded diamond cup wheels and mounted points were used to drive abrasive slurries. A few blades of fair quality were machined using the mounted point system but the stock removal rate was found to be too low to be commercially feasible. In this study, a single blade took four hours to machine and cost $319, thus 150 hours and $12,500 would have been needed for a 30 blade wheel **(78)**.

Precision grinding of irregular shapes requires less expensive small diameter diamond wheels. Contour grinding, cam grinding, and pantograph profile grinding allow close tolerances to be maintained on finished parts. Low initial costs are offset, however, by very slow material removal rates. Product size control is primarily dependent on the skill of the operator running the equipment **(68)**.

The need for finish machining (especially with diamond tooling) should be minimized or eliminated where possible; this may be accomplished by molding or casting parts to size (a major drawback of hot pressing), or by machining components in the unfired or "green" state if possible. As a general rule, dimensional tolerances can be maintained no closer than one percent by green machining of those ceramic materials having normal sintering shrinkage **(79)**. Any surface grinding marks or striations introduced into the surface during green machining (with conventional steel or carbide tooling) are not injurious to strength once the material is sintered at high temperature to its final shape - a major advantage of green machining.

Electrical Discharge Machining

EDM is a process that removes material from any electrically conductive workpiece by the erosive action of high frequency spark discharges. Since the spark fires across the narrowest gap between the electrode and workpiece, the erosion (actually vaporization) has a "leveling" action that creates a uniform pocket around the electrode as it is advanced into the workpiece. The shape of the cavity thus formed conforms almost exactly to the mating shaping of the electrode, or tool. Tolerances of ± 0.013 mm (± 0.0005 in) are routinely attainable, and with care can be maintained to ± 0.005 mm (± 0.0002 in) **(80)**. As the cut is being made, there is some wear that occurs on the electrode, thus the use of EDM for mass production will necessitate having a supply of identically shaped electrodes available if output is to be kept dimensionally consistent **(80)**

EDM has the ability of making complex cuts in the hardest of materials, the only requirement is that the material being machined must be electrically conductive. Hot pressed silicon carbide has been successfully machined by EDM, however, the surface of the finished test samples was severely damaged. In a study by the Ford Motor Company this surface degradation was enough to cause a 54% reduction in strength compared to conventional diamond ground samples **(81)**. Since each spark impact actually produces melting and vaporization of the surface material, the resulting machined surface is not representative of the bulk material - a detrimental aspect of EDM that certainly must be recognized **(80)**. It may be possible to machine other electrically conductive ceramics such as boron carbide and graphite, or to green machine silicon metal precursors before nitriding using EDM.

A variation of conventional EDM uses wire traveling from reel to reel instead of a shaped tool for the electrode. The wire advances gradually between reels to compensate for wear that occurs at the point of cut. This variation of the process amounts to what is essentially an electronic bandsaw **(82)**. Previously, this type of EDM equipment was used as little more than a slicing machine. Now, complex two-dimensional shapes can be cut using numerical control positioning. EDM can thus be put to work on simple profiling jobs without the necessity of special electrodes **(80)**.

In the future, EDM will probably not gain widespread use in the ceramic machining industry, primarily because of the surface damage induced in the workpiece, the relatively slow speed of the machining process, and because of the stipulation that the workpiece be electrically conductive.

Electrochemical Machining

ECM, like EDM, requires that the workpiece be electrically conductive The workpiece is connected to the positive terminal of a d-c power supply. A tool, or cathode, connected to the negative terminal, is advanced toward the workpiece through an electrolyte that completes the electrical circuit between anode and cathode **(83)** Current flowing through the electrolyte (usually sodium chloride solution) ionizes the positive workpiece and causes surface atoms to migrate toward the cathode (reverse plating). Before they can reach it, they are washed away by the fast flowing electrolyte **(84)** The success of an ECM cutting action depends a great deal on maintaining a correct flow of electrolyte through the gap between tool and workpiece - the focus of much electrode design effort

ECM delivers excellent surface finish and induces less surface stress than conventional drilling Little heat is involved ECM is good for relatively high production jobs, the electrode does not change shape and can be used over and over ECM is faster than EDM, but it is less accurate **(80)**. The dimensional accuracy that can be maintained with ECM depends upon whether the particular features in question are to be formed by the frontal surface of the tool or whether they are located on the sidewall of the bore. Tolerances as tight as ± 0.008 mm (± 0.0003 in) are not uncommon on features formed by tool frontal surfaces. On cavity sidewalls, tolerances on the order of ± 0.05 mm (± 0.002 in) can be held **(83)**.

ECM has become very important to the aerospace industry for the machining of hard, exotic metal alloys for use in jet engines. The application of ECM to ceramics will be limited to the few which are good electrical conductors, and to silicon powder precursors prior to nitriding. Such "green" machining of silicon may become a very important application of ECM in the future.

Ultrasonic Abrasive Machining

This method of machining is particularly suited for the machining of hard ceramics; in fact, the harder the workpiece to be machined, the faster the cutting action obtainable. Abrasive grains are the cutting edges of the tool. They are carried, in a recirculating liquid slurry that flows between the workpiece and the tool—coarse grit for rapid cutting, and finer grits for finishing **(85)**.

Abrasive grains bombard the workpiece, driven by the linear oscillation (approx. 20,000 times per second) of the tool. The shape of the tool determines the precise bombardment pattern of the grit against the workpiece **(85)** Tools are made from ductile, high strength materials to minimize tool wear Most often, stainless steel or brass is used.

Ultrasonic machining is a non-thermal, non-chemical, non-electrical process, consequently there can be no change in the microstructural, chemical or physical properties of the material being machined Ultrasonics will machine tapered, through, and blind holes or slots, can perform multiple "drilling", slicing, dicing, or engraving, all using easily made tools The precision and finish of ultrasonic machining depends on the size and finish of the tools, fineness of the abrasives, and on the material being machined In roughing operations, based on the material, a 25 microinch finish may be obtained with 240 grit A 10 micro-inch finish requires up to 800 grit Tolerances of ± 0 025 mm (± 0 001 in) are generally obtained with 240 grit and tolerances of ± 0 013 mm (± 0 0005 in) or better may be obtained with finer abrasives as secondary operations **(85)**.

Ultrasonic machining is useful in applications such as cutting a form, e.g., sinking a design in a hard carbide die. The design may be cast, molded or machined in an easily worked material such as brass, which can then be used as the tool to generate the identical pattern in a hard or brittle material **(86)**.

The Ford Motor Company has successfully used ultrasonic machining for the rough cutting of constant cross section airfoils from billets of hot pressed silicon nitride **(87)**. Tool wear during this operation was approximately one part tool to three parts silicon nitride. However, this wear ratio was only characteristic of the particular tool material used, the material being machined and the shape of the machined part; not all ultrasonic machining operations exhibit the same tool-part wear ratio. Attempts by Ford to machine airfoils with the desired taper and twist from the rough have thus far been unsuccessful. However, ultrasonic machining of the contoured disk area from hot pressed silicon nitride has been successfully performed **(81)**.

AiResearch, using ultrasonic machining for the production of single rotor blades from hot pressed silicon nitride, has observed only a 1:100 tool-part wear ratio. From this study it was concluded that the most cost effective way of machining hot pressed silicon nitride with retention of mechanical properties was by using a combination of ultrasonic machining, form wheel grinding, and profile grinding. Further development will lead to increased cost reduction through more extensive use of ultrasonic machining **(88)**.

Of all the machining methods currently employed for machining brittle materials, ultrasonic abrasive machining appears to hold considerable advantage, tooling is easy to make and is inexpensive, secondly, surfaces are minimally damaged by the abrasive impact, displaying no directional machining effects, and thirdly because the method [illegible] the machining of complex shapes that [illegible] ot be machined economically by any [illegible]

Economics of Ceramics

Raw Materials

Ceramics have long been considered for application in the hot path of a gas turbine engine, candidate materials have been compared individually in preceeding sections. In detailing costs of ceramic raw materials, however, the literature has been somewhat deficient, and has to a large extent unconsciously portrayed turbine ceramics as traditional ceramics - "that which is dug up from the earth and burned", instead of as highly-refined, technical products. Such misconceptions are forgivable, and will diminish as time brings such materials out of the laboratory and into the reality of being marketed within a workable, efficient engine. Once such materials have been thoroughly tested by those organizations dedicated to marketing a ceramic gas turbine engine, and judged as technically practical, more comprehensive economic evaluations related to mass production will certainly follow. It must be emphasized that neither silicon carbide nor silicon nitride can in themselves be considered to be raw materials, not even in low-grade, impure form they do not occur naturally as SiC or Si_3N_4

Reaction bonded silicon nitride is a product of the nitridation of silicon metal Impurities in the starting silicon must be minimized for best oxidation resistance at elevated temperatures Kawecki Berylco maintains a 99 plus percent purity in the starting Si, bought in lump form for $0 50 per pound **(89)**. Silicon metal of 98-99 percent purity may be produced by reducing silica (quartz, quartzite, sandstone or quartz sand) with charcoal in an electric low shaft furnace **(90)** (silicon never occurs uncombined in nature) Silica is one of the [illegible] abundant of all materials and in combined [illegible] uncombined states is estimated to form 60 percent of the earth's crust **(91)** High quality silica deposits in the United States will sustain the silicon and ferrosilicon industries indefinitely, based on present requirements **(91)** Silicon supply and production are related primarily to the requirements of the steel and aluminum industries, and its price is influenced by the cost and availability of transportation and energy **(91)** *The price of silicon has not fluctuated substantially during the past two decades* **(91)** However prices did increase somewhat in 1974 because of the higher costs of scrap iron (for ferrosilicon production), metallurgical grade coal, electric power, and the cost of newly-installed devices for pollution control such as baghouse and water purification plants **(91)**. Commodity prices are now steady, ranging from $0.425 per pound for Si containing 1% Fe/0.07% Ca to $0.464 per pound for 0.35% Fe/0.07% Ca **(92)**.

Amorphous, submicron-sized silicon nitride powder, a necessary starting material for producing silicon nitride by sintering, is derived via the vapor sublimation of reaction bonded silicon nitride. Consequently, both are dependent upon silica as a basic raw material. Direct sintering of submicron-sized silicon nitride is not possible without the use of a sintering aid (see Section on Sinterable silicon nitride). For this reason the Si_3N_4 powder is usually combined with 4-17 wt. percent yttrium oxide (Y_2O_3) **(93)** in order to achieve high densities and good high temperat[illegible]erties (compared to Si_3N_4 + MgO).

Domestic and foreign reserves of yttrium are large and sufficient for several hundred years at current rates of demand, and the industry has the capability to meet any foreseeable increases in demand **(94)**. Most domestically-purified yttrium is extracted from imported yttrium-rich residues that are recovered during the processing of certain Canadian uranium ores **(94)**, although the mineral monazite (largely from Australia and Malaysia) and xenotime (processed in Malaysia and Japan) are the major world sources of yttrium **(95)**. Yttrium mined in the United States supplies less than one half of domestic requirements, however large U.S. resources of phosphate rock and tailings from certain iron ores could be processed for yttrium and heavy subgroup rare-earths if sufficient demand should develop **(94)**. At $34.50 per pound for color television phosphor grade (99.9 + purity), Y_2O_3 is not cheap **(96)**. As a sintering aid in silicon nitride, however, 97% minimum purity should be acceptable such a commercial grade would probably sell for $20 per pound **(97)** As a sintering aid, at only 4-17 wt. percent per part made of sintered Si_3N_4, the price becomes more acceptable As industry starts to consume more of the rare earth metals, selling prices may decrease during a period when the prices of almost all other metals are rising **(95)**

Silicon carbide is produced by heating silica with an excess of carbon (usually coke) in the presence of sawdust and salt in an electric furnace. The salt forms volatile chlorides with iron, aluminum, and other impurities while the sawdust promotes porosity which allows escape of the gases **(91)**. Typically, in what is known as an Acheson furnace, the raw materials are piled over a graphite resistance element and heated at temperatures ranging from 1649°-2205°C (3300°-4000°F). Distinguishable, concentric regions of purity ranging from 98% SiC at the outer layer, to 99.7% SiC closest to the graphite rod are formed. The higher purity material nearest the center is utilized by the Carborundum Company in producing sintered α-SiC **(64)**. Carborundum is currently producing α-SiC on a small commercial level and is constructing a facility to process tonnage quantities of sinterable SiC powder into prototype shapes and parts **(12)**. The raw materials—silica coal (for coke), salt, and sawdust are usually priced on a per ton basis, however, the combined cost of all four works out to less than $0.05 per pound (for the mixture), even if anthracite coal is used to make the coke (anthracite is approximately 2½ times more expensive than bituminous). Such a price is representative of the raw material cost at the mine or other place of origin. Shipping costs, even in bulk, of most ceramic raw materials represent a substantial portion of the final cost to the purchaser **(79)**, and in this particular case would undoubtedly represent the major portion. Delivered, such raw materials cost from $0.40 to several dollars per pound **(98)**. Additionally, estimated at 10% of the basic raw material cost, is the cost for sintering aids and organic binders for Carborundum sintered α-SiC **(64)** Silicon carbide produced by infiltrating carbonaceous precursors with silicon, is estimated to be twice as expensive as the sintered α-SiC, because of higher costs for the silicon metal **(99)**

It may be concluded that the cost of the raw materials used in producing SiC and Si_3N_4 turbine ceramics is in general, very low, attributed not only to the relative abundance of the raw materials, but also to their existence in nature as high-grade deposits. There is little (if any) overburden to remove in uncovering the deposits, nor are the desired materials locked in with large amounts of impurities A possible exception to this rule is yttria, which does require some upgrading from the monazite (55-65% rare earth oxide), xenotime (minimum of 25% Y_2O_3) and uranium processing residues (about 25% Y_2O_3), however this presents no problem. Nickel base alloys, for example, require that 100 tons of ore be dug up in order to produce one ton of nickel **(100)**; such problems do not exist in mining raw materials for Si-based turbine ceramics. The ceramics industry can rely in large part on local supplies of high-grade mineral products which require a minimum of processing. The metals industry, on the other hand, must rely on progressively lower grades of ore which must be transported for increasingly longer distances from source to mill **(101)**. Both the upgrading and transportion of low grades of metal ore will mean the energy content (and hence the cost) of delivered ore must rise much faster than the delivered costs of ceramic raw materials **(101)**.

Processing Economics

Because of the nature of most ceramic processing methods employed in the production of turbine ceramics, i.e. fabrication from a powder vs. forming from a melt as in most metal-related processes, deliberate steps must be taken to crush, comminute, screen and size the ceramic raw materials after they are received from the source. Such operations are usually highly automated and represent a relatively small portion of the cost of the entire production process.

Next, additives, plasticizers, and other organics may be blended into the sized powder, which is then followed by some sort of forming into the desired shape. Fabrication methods which appear to be most promising for high volume mass production at low cost are die pressing, slip casting, injection molding, and extrusion of the powder to a "green" shape, followed by green machining (if necessary), then sintering to the final part shape. Hot isostatic pressing has perhaps the highest potential for low cost part fabrication **(24)** of extremely high strength, high Weibull modulus silicon nitride. However, at this time such technology is limited to a single source **(102)** (with other laboratories quickly becoming involved), which has generated some very promising, although publicly unsubstantiated, data. Chemical vapor deposition, although interesting in concept, has not yet produced a stress-free, flaw-free rotor shape, and even if it were possible, the process is time consuming and therefore expensive. Hot pressing, as it now stands, is prohibitively expensive because of high tooling costs, because it is time consuming, and because of the limited part geometries that can be directly pressed without some sort of final machining. Only forming techniques that permit high volume production of complex shapes can and will be considered in the future.

The manufacturing capactiy of such materials as SiC, Si_3N_4, and ceramic regenerator materials such as LAS, MAS, and AS, have up to now been limited to research and development-type quantities, i.e. for prototype engine parts and for test samples. Costs have usually been high for such experimental materials, which are often made by hand one at a time. The ceramics industry traditionally has been a model industry in the field of highly automated, efficient production processes with its large batch mixing houses, logical and fast station-to-station routing of ware, and energy-saving tunnel furnaces. What is needed is a breakthrough by researchers devoted to SiC and or Si_3N_4 technology, specifically demonstrating that a turbine rotor can be produced via a potentially cost effective fabrication process and that is also capable of long-term survival in the severe environment of the gas turbine hot path. Such a breakthrough would arouse not only interest but commitment from those organizations presently evaluating the potential of a ceramic engine, and would be a key factor in opening the door to large scale manufacturing of turbine ceramics. Once a marketable product has been demonstrated, manufacturing capacity will be dependent primarily upon transportation of goods to and from the plant, a stable labor supply, and a reliable source of (preferably) low cost electrical power. None of these are foreseeable problems in the future due to the wide distribution of low cost, high purity raw materials across the United States. Manufacturing capacity of turbine ceramics is limited now; assurance of long-term demand for a marketable product will be the incentive for ceramic manufacturers to expand toward high volume production facilities, forcing unit part costs down.

Detailed analyses of energy consumption has become increasingly important for the ceramics industry, particularly in the last five years during which time a significant number of corporations have faced fuel shortages. Possibly because of the very visible way in which the ceramic industry consumes most of its energy, i.e., in kilns and furnaces, it is assumed by many that the energy consumption must be extremely high **(101)**. What is not understood is that the route from raw materials in the ground to finished product is, in most instances, short **(101)**. Figure III-6 **(101)** is a comparison of energy inputs/lb of product for various ceramic products, the information being compiled by Battelle, Columbus Labs in a study done for the Federal Energy Administration. These values may be compared with the energy inputs/lb. of various metal and polymer products in Figure III-7 **(101)**. The amount of silicon carbide produced per KWh varies with quality of product, however, an energy input of 2.86 KWh/lb (9760 Btu/lb) is reasonable for an average grade of Acheson furnace SiC grain **(103)**. Once the SiC grain is produced, additional energy consumption per pound of sintered SiC should be only slightly higher than that of the whiteware-refractories industry, primarily because of the higher furnacing temperatures necessary for densification—approximately 2200°C (4000°F). Maintaining a furnace at such a temperature is not expensive (from an energy viewpoint) so long as the furnace is well insulated and is not thermally cycled. It would be expected that energy requirements for the production of sinterable SiC would be comparable to those of the glass industry (on a per pound basis). Siliconized SiC production and all forms of Si_3N_4 would be expected to consume slightly more energy per pound of product (reduction of SiO_2 to form Si metal), however in large-scale production energy costs per pound of product should remain less than for those of an alloy steel.

Perhaps the greatest expense in a ceramic manufacturing process is machining costs, particularly if necessary after final densification. In this respect, those materials which can maintain reproducible final part dimensional tolerances by way of economical forming methods and still fulfill the job requirements, will undoubtedly command a considerable advantage. Material shrinkage, if any, on sintering will need to not only be uniform, but predictable: unfired or partially densified ("green")

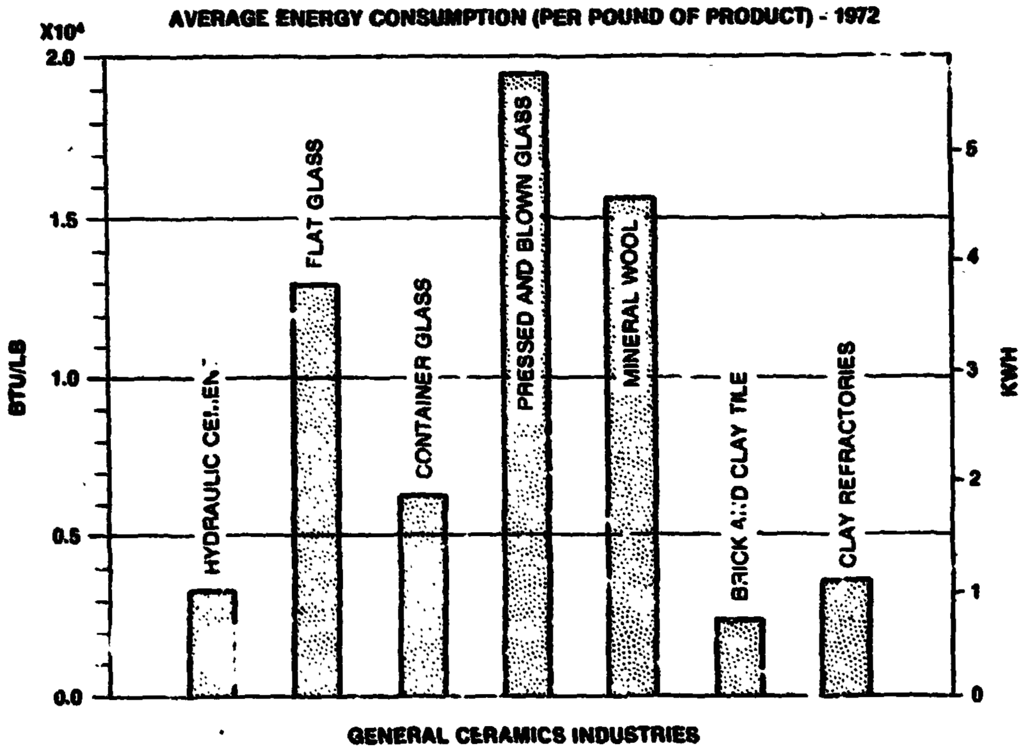


Figure III-6 From Battelle, Columbus Labs Study for FEA (Ref. 101) machining may be necessary in many instances in order to avoid the more expensive diamond or ultrasonic abrasive machining required on the extremely hard, fired product (SiC or Si_3N_4). For this reason, it is extremely doubtful that conventional hot-pressing, followed by time-consuming machining, can survive as a mass production fabrication process for turbine ceramics. Additional research is needed to better evaluate the potential of sintered α -SiC, sintered Si_3N_4, and hot isostatically pressed Si_3N_4 in those highly stressed applications (esp. turbine rotors) where until now only hot pressed Si_3N_4 has been evaluated

In gathering all the vague details from each particular phase of the manufacturing process for turbine ceramics, and then attempting a dogmatic assignment of cost per unit pound of ceramic, even the most meticulous student of the literature will soon find himself assigning dollar signs to words *and then trying to somehow combine these with the* few numbers accessible to him at the time. Final manufacturing costs per part are dependent on many factors that are difficult to fully assess at this time some of which include

1. The **volume** (quantity) of parts produced - How many parts in how many engines will be produced initially? What is the percentage increase each year of new cars equipped with the ceramic turbine? Component part costs should decrease with increased manufacturing capacity.

2. What **method of fabrication** would be used for each particular part? Each method of fabrication involves a different capital investment initially, as well as different operating costs. How long do injection molds for abrasive ceramic materials last? How many parts can be slip cast in each plaster mold? Each particular part may have more than one method of fabrication. What do the parts look like - which fabrication method is best?

3. The amount of **machining** that will be required It is hoped that this operation could be minimized, or eliminated if possible, however, a conservative estimate of cost must include some green and or final machining - which will it be, on which material, and how much must be removed?

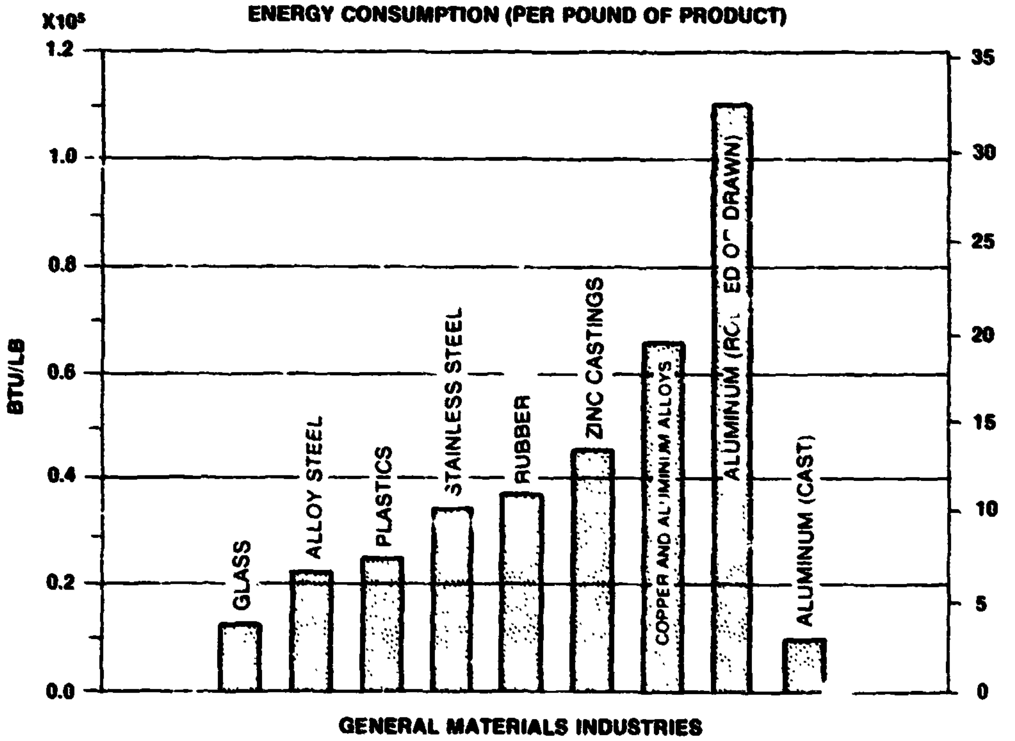


Figure III-7 From Battelle, Columbus Labs Study for FEA (Ref 101)

4. Whether **proof testing** or other **non-destructive testing** will be required. It is highly probable that some will be. If so, will every part be checked or just a random sampling? Will every turbine rotor produced need to be spin tested? If so, it will be reflected in the final part cost. What other non-destructive tests will be available in the future? Are present NDE methods satisfactory for the future?

The answers to the above questions are vitally important, along with many others like them, if a clear understanding of manufacturing costs of ceramic turbine components is to be obtained. As the infant technology continues to develop, one by one such questions will be resolved, but it will take time. It is clear, however, that the material content of any component cost is significantly lower when using ceramic materials than when using superalloys **(37,104)** - probably at least by an order of magnitude **(105)**. As has been pointed out, however, the major part of a components' cost will be in the process rather than the material, and as such is amenable to reduction by production engineering for high volume throughputs **(104)**. An example of **costs experienced now** for production of reaction bonded silicon nitride **(89)** is shown to be a function primarily of fabrication technique and quantity of parts produced:

Injection Molding - $5 - $1000 per pound (finished part cost). A tool with repetitive part reproducing represents the minimum part cost whereas a low-volume, very complex tool may cost $1000 per part.

Iso-pressed/machined - $25 - $1000 per pound. Cold isopressed silicon, then machined. Almost always faced with some machining cost.

Slip Casting - $25 - $80 per pound. Cast parts limited in shape; very attractive for simple, hollow parts

Finished part costs may decrease in the future, hopefully below those listed above; although it is impossible to speculate as to how much lower "Inexpensive", in ceramics economics, may be a part that costs about $4/lb **(98)**

Whatever the future cost per pound of a ceramic component, or for that matter the comparative component cost of a superalloy or refractory metal part, it is important to include also a comparison on a basis of cost per unit volume of product.

Silicon carbide and silicon nitride (densities ranging from 2.5 - 3.2 g/cm^3 depending on fabrication process) are approximately 55-65 percent lighter per unit volume than the superalloys (density $\approx$ 7.0 g/cm^3). Given equal amounts of ceramic and metal, weightwise, the volume of ceramic would be 220-285 percent greater. Since two to three times as many parts can be made with a pound of ceramic compared to a pound of superalloy, a 200-300 percent price disadvantage (cost per pound) for ceramics, if ultimately found to be necessary, would in actuality be no disadvantage at all. Following similar lines of thought, if the technology can be developed for high capacity manufacturing of ceramic turbine components while maintaining a price per pound equal to that of a similar metal part, because of the density correction ceramics would actually enjoy a considerable cost advantage. Perhaps the traditional concept of cost on a per pound basis has become obsolete.

The issue of cost of the ceramic components now being considered for the hot zone of a gas turbine engine must be placed in proper perspective. In contrast with standard economic considerations which emphasize the importance of final part cost, on a Return On Investment (R.O.I.) basis, the initial price of the uncooled ceramic components is practically irrelevant. The single shaft turbine vehicle is projected to better the fuel economy of an equivalent Advanced Otto-engined (gasoline piston engined) Compact car by 32%, and the free-turbine version by 38% on the Federal Driving Cycle Urban test The corresponding gains over the FDC Highway are about 53% (SS) and 40% (FT) **(106)** R.O.I considerations may best be applied to the key engine components which allow this kind of savings to a single owner over the course of his vehicle's lifetime, or to the combined annual fuel savings of a nationwide fleet of such ceramic-equipped vehicles Such savings would justify an all-out assault on the technical problems that still impede utilization of the new ceramics **(107)**

High Stress, High Temperature Parts

The following materials listed in order of greatest immediate potential, are now being given careful consideration for use at high stress, high temperature locations within a marketable gas turbine engine It should be emphasized that none of the following have properties which have, to date, been completely optimized—they are all at the R/D stage

1. Hot Isostatically Pressed Silicon Nitride

Believed to offer the greatest potential for high strength and Weibull modulus of any material presently under consideration. This fabrication process is economial for high volume quantities of complex parts. Although the process is still in the developmental stage, and is experiencing minor problems with canning and equipment, such problems are not regarded as insurmountable, and should be resolved within the next few years. Silicon nitride produced by the H.I.P. process is considered to have the greatest potential for survival as a turbine rotor, spinning at 1370°C (2500°F) within a marketable gas turbine engine, and deserves a more intense research effort than that currently being expended.

2. Sintered Alpha Silicon Carbide

Made from submicron sized α-SiC powder exclusive to the Carborundum Company, Niagara Falls, N.Y., this candidate has demonstrated steadily increasing strength since its introduction two years ago, due primarily to better powder processing control A concentrated effort is now underway, the goals of which are to better assess the specific fabrication processes that may be used to produce complex shapes from sintered α-SiC that will minimize or eliminate final part machining, and to increase the material's Weibull modulus through the implementation of better process controls The material has unequaled oxidation resistance compared to other forms of silicon carbide or silicon nitride, and has actually demonstrated an increase in strength with increasing temperature between 25°C (77°F) and 1650°C (3002°F) Although the material has a relatively high thermal expansion coefficient when compared with silicon nitride, its higher thermal conductivity, in combination with sound design principles may be enough to offset this contribution towards lowered thermal shock resistance. It remains to be seen whether this can indeed be accomplished.

3. Sinterable Silicon Nitride

Most often utilizing Y_2O_3 as a sintering aid, this material also offers the potential for low cost part fabrication, minimizing or eliminating the need for final machining. Extensive work is being done by researchers toward increasing sintered density (and consequently room temperature strength) while at the same time minimizing the inevitable strength decrease with increasing temperature that results when sintering aids are added to Si_3N_4. Better control of temperature, atmosphere, and pressure during furnacing has resulted in improved final product properties. Progress in sintering of silicon nitride should be carefully monitored in the future.

4. Chemical Vapor Deposited Silicon Carbide

CVD SiC is an attractive candidate for service in the hot zone of a gas turbine engine because of high strength at elevated temperature, high density, minimal final machining necessary, good surface finish and minimal creep and oxidation rates. Unfortunately, very serious fabrication problems such as poor vapor flow control, residual stresses which causes cracking of the as-deposited material, and flaw size and flaw density continue to hamper developmental progress on CVD SiC If and when such problems are resolved, CVD SiC will receive much greater attention as a potential gas turbine engine material

5. Sinterable Beta Silicon Carbide

Displaying many of the fine properties of sinterable α-SiC, this material, developed by the General Electric Company has recently received much attention Preliminary problems such as uncontrolled grain growth and β-α transformations at elevated temperature appear to have been resolved A major problem remains in that there is now no commercial source of β-SiC powder available This in itself considerably diminishes the chances for utilization of β-SiC within a marketable gas turbine engine

6. Hot Pressed Silicon Nitride

To date, in a Ford duo density axial turbine rotor, this material, HPSN, has been the only material that has come close to surviving the high centrifugal loads which current turbine design requires. The strength of this material is exceptionally high at room temperature, falling off quite drastically at 1370°C (2500°F) thus necessitating the duo density (RBSN blade ring/HPSN hub) design. However, even if properties of HPSN could be developed which would not decrease with temperature, the hot pressing process for fabrication of dense material would still remain prohibitively expensive and time consuming. Only simple shapes have been hot pressed to date, these requiring final machining (typically with diamond tools) in order to fabricate the desired part shape. Graphite pressing dies are expensive and generally not reusable. Since this process does not lend itself to high volume production, it is extremely doubtful that this method of fabrication will be used by the automotive industry for future turbine engine parts.

7. Hot Pressed Silicon Carbide

For the same reasons given for HPSN, and because hot pressed SiC is not as strong or thermal shock resistant as HPSN, HP SiC should be given little consideration for gas turbine engine application.

Medium Stress, High Temperature Parts

For high temperature stationary parts within a ceramic gas turbine engine, superior strength will not be as important a factor as general high temperature stability and the ability to remain functional after thousands of thermal cycles. It has already been demonstrated that many of these positions can be successfully filled with present day ceramics, again the silicon carbides and silicon nitrides being most successful. Undoubtedly, for such applications, there will be a number of materials with qualifying physical properties; for this reason it is believed that economics will play an important role in deciding which candidate(s) will ultimately be chosen. Conventional low cost fabrication methods which minimize final machining [illegible] emphasized. It is doubtful that any one material [illegible] dominate the field, unless it has a [illegible] outstanding cost advantage. Likewise, it [illegible] believe that a higher strength material capable of low cost fabrication would not be chosen. Such a material as sintered α-silicon carbide may very well fall into this category, as well as HIP silicon nitride or sintered silicon nitride, if such materials prove to be cost competitive and are also formable into the required design geometries.

Some materials now considered to be medium-stress candidates may very well, given additional research and development time, promote themselves into the "high-stressed" category (i.e. Si/SiC composites or the sialons). Materials under consideration now as medium-stressed candidates are: 1. Recrystallized SiC, 2. Reaction sintered silicon carbide, 3. Reaction bonded silicon nitride, 4. Si/SiC composites, and 5. SiAlON, not necessarily in order of greatest potential for success.

Recrystallized silicon carbide and reaction bonded silicon nitride do hold a possible advantage in that they exhibit no strength degredation with increasing temperature up to 1400°C (2552°F) although their strengths are not exceptionally high to begin with. Oxidation resistance is dependent mainly upon impurity levels (higher levels of impurities, particularly in reaction sintered silicon nitride, tend to produce a thick glassy coating at elevated temperature).

Reaction bonded silicon carbide and Si/SiC composites have the disadvantage of a second phase of silicon metal which causes a strength decrease at elevated temperatures. It will be important to limit the temperature at which these materials operate. They have, however, demonstrated the ability to withstand thermal fatigue cycling in experimental engines and test rigs due to the stress-relieving silicon phase. Future cost of the Si/SiC composites is uncertain, and is primarily dependent upon the cost of carbon fibers in bulk quantities. Si/SiC composites have a very high potential both for improved strength and for improved fabrication capability.

SiAlONs although offering the potential for pressureless sintering to full density, for flexible fabrication capability, and for developing high strength, are presently at an infant stage of development. There remains a tremendous amount of basic research to be done, particularly involving the system's phase equilibria, before they can be considered exploitable for use in an all-ceramic gas turbine engine

Low Stress Parts

Presently, the ceramic regenerator may be considered to be the most well-established demonstration of ceramic practicality in a gas turbine engine. This application demands excellent thermal shock resistance combined with resistance to chemical attack, rather then high strength. At this time AS (aluminum silicate) and LAS/MAS (lithium aluminum silicate/magnesium aluminum silicate) compositions offer the greatest advantage. Conventional LAS is highly prone to chemical attack by sulphur in fuels and road salt, but does have a very low thermal expansion coefficient giving it good thermal shock resistance. Conversely, MAS is chemically stable but more subject to thermal fatigue failure.

Ceramic Processing Requirements

Coatings for Oxidation/Corrosion Protection

Coatings for oxidation/corrosion protection are unnecessary for sintered silicon carbide, chemical vapor deposited silicon carbide, or for hot pressed silicon carbide. Forms of silicon carbide which contain free silicon are subject to oxidation of the surface, however, this may be considered protective rather than destructure. Hot pressed silicon nitride may benefit from a surface layer of pure CVD silicon nitride, however, such work is inconclusive. It is highly unlikely that any coating would significantly benefit the varieties of silicon nitride containing sintering aids; strength degradation is primarily a result of intergranular glassy phase formation, and to a lesser degree because of oxidation from the surface.

Joining Methods

The science of joining of ceramics to ceramics and ceramics to metals is diverse and offers the designer with a wide assortment of options, but also many restrictions. There is a great need for additional research in this area.

Silicone rubber is attractive as a sealing or gasketing material below 260°C (500°F). Epoxies, both filled and unfilled display a wide range of strengths, 28-140 MN m^2 (4000-20,000 psi) tensile, but rapidly deteriorate at temperatures greater than 260°C (500°F). Polyimide adhesives are strong and resist thermal degradation better than the epoxies, but will only survive 1[illegible] hours at 370°C (700°F). Ceramic adhesives (inorganic cements) are not plagued by temperature restrictions but such bonds are very weak - less than 6.9 MN m^2 (1000 psi).

Mechanical bonding generally offers greater physical stability and durability to the joint than do the organic and inorganic adhesives, however, if point stresses are not minimized, such joints will prematurely fail. Special effort must be directed toward cushioning bolt heads, clips, clamps, springs, etc.

Solid phase joining, such as diffusion bonding, gas pressure welding, inertia welding, or ultrasonic welding offer considerable future potential, particularly if the ceramic must have strength and stability at high temperatures.

Liquid phase joining, i.e. brazing or welding of crystalline ceramics is an area toward which much research has been and still needs to be devoted. Usually metallizing is necessary before attempting to braze or weld in order to facilitate good wetting of the joining material. Often, the braze material may be a slurry of constituents very similar to the materials being joined. Such a joint may be reaction sintered or diffusion bonded at high temperatures to effect the bond. Extensive experimentation is still required in order to find the best methods of joining turbine ceramics to themselves and to metal. Additional research is desperately needed.

Machining Methods

Final-part machining operations, if necessary, will add considerably to the final product cost of hard ceramics. If possible, "green" machining should be performed on such a part if specifications do not require maintaining tolerances closer than ± 1% after sintering. If closer tolerances are required, final machining will be necessary. Two methods are most effective: 1. Diamond machining and 2. ultrasonic abrasive machining. Diamond machining is, for all practical purposes, restricted to cutting of simple straight slots, slicing, or round holes. Finish diamond grinding of surfaces is more time-consuming, and introduces surface flaws which may have a detrimental affect on the strength of the material being machined. Advantages of ultrasonic abrasive machining are that it is a non-thermal, non-chemical, non-electrical process, consequently, there can be no change in the metallurgical, chemical, or physical properties of the material being machined. This method lends itself to the machining of complex shapes that very often cannot be machined economically by any other method.

Electrical discharge (EDM) and electrochemical (ECM) machining are not effective for machining low-conductivity SiC and non-conductive Si_3N_4, but may be very important in machining Si metal precursors prior to nitriding.

Economics of Ceramics

Raw Materials

Cost of raw materials required for those ceramic candidates for gas turbine engine application is generally very low. Primarily, this is due to their abundance in high-grade deposits, which require a minimum of processing. Silicon metal, used for producing silicon nitride, as a product of the reduction of silica (SiO_2), now sells for \$0.42 - \$0.46 per pound depending on purity. Sintering aids such as yttria (Y_2O_3), when needed, or other less expensive oxides, are abundant and will not be prohibitively expensive when used in relatively small weight percentages of the bulk Si_3N_4-based product.

Raw materials for silicon carbide production (silica, coke, sawdust, and salt) combined are less than \$0 05 per pound. Siliconized (silicon metal infiltrated) products may be slightly more expensive from a raw materials cost viewpoint.

Transporation costs, even in bulk quantities, from mine to fabrication plant, will represent the greater percentage of raw materials cost and may drive the price to \$0.40 or even to several dollars a pound. The United States is endowed with virtually unlimited quantities of all raw materials needed for gas turbine engine materials except yttria, although yttria is readily available from neighboring Canada as well as a number of other world sources.

Processing

Economical fabrication methods for ceramics include, but are not limited to, die pressing, slip casting, injection molding, and extrusion, followed by reaction sintering, conventional sintering, or hot isostatic pressing (HIP). If machining is necessary, it should be done in the "green" (unfired) condition if costs are to be minimized, since the greatest expense in the ceramic manufacturing process will undoubtedly be machining costs. In this respect, those candidates which can ultimately maintain reproducible final part dimensional tolerances by way of economical forming methods and still fulfill the job requirements, will command a considerable advantage.

Variables which are difficult to fully assess at this time, and which are critical in determining final part costs are: 1) the volume of parts produced, 2) the method of fabrication for each particular part, 3) amount of machining needed (and by what process) and 4) the amount of non-destructive testing and/or proof testing which will be required. It is expected that energy requirements for the production of ceramic components should remain significantly less than those for the production of metal alloys.

While at first glance it may appear that ceramics could become more costly than superalloys (on a cost per pound basis) since there are so many potential variables, consideration should be given to the density correction (ceramics are only about 40% the density of superalloys) which may allow ceramic components to actually enjoy a cost advantage if compared on a cost per unit volume basis.

Finally, the issue of ceramic part costs should be put into proper perspective. Return on Investment (R.O I.) considerations should be applied to the key ceramic components which will allow as much as a 53% increase in fuel economy (highway) of a single shaft turbine-engined vehicle compared to an equivalent compact car equipped with a conventional gasoline piston engine. Such savings would seem to justify an all-out assault on the technical problems that still impede utilization of the new ceramics.

William L. Ehlers
March, 1978

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