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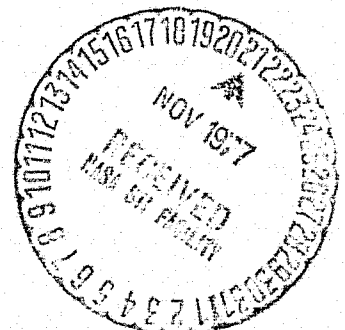
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**IMPROVED PERFORMANCE OF SILICON NITRIDE-BASED
HIGH TEMPERATURE CERAMICS**

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ABSTRACT

Work under four NASA contracts to improve Si_3N_4 based ceramics will be reviewed: (1) High temperature strength and toughness of hot pressed Si_3N_4 were improved by using high purity powder and a stabilized ZrO_2 additive, (2) Impact resistance of hot pressed Si_3N_4 was increased by the use of a crushable energy absorbing layer, (3) The oxidation resistance and strength of reaction sintered Si_3N_4 were increased by impregnating reaction sintered silicon nitride with solutions that oxidize to Al_2O_3 or ZrO_2 , (4) Beta prime SiAlON compositions and sintering aids were developed for improved oxidation resistance or improved high temperature strength.

INTRODUCTION

About 30 years ago the NACA (National Advisory Committee on Aeronautics) the forerunner of NASA (National Aeronautics and Space Administration) embarked on a program to develop a new class of materials for turbine blades. They were called cermets, a combination of ceramics and metals. They were intended to have the advantages of both types of materials, that is, the high temperature strength and oxidation resistance of ceramics and the ductility of metals. Unfortunately they had the brittleness of ceramics and the low oxidation resistance of metals. Moreover, that was before the day of 3D finite element computer programs to handle stress analysis. And furthermore, the knowledge of designing with brittle materials was not very sophisticated. As a result of the lack of success with cermets, NACA gave up on cermets and concentrated its efforts on developing superalloys as turbine materials.

Toward the end of the 60's the British began to develop silicon nitride-based ceramics and new interest was generated in the use of structural ceramics as turbine components. Interest at NASA was revived, and we applied our experience in high gas velocity burner rig testing of superalloys to the evaluation of ceramics. Figure 1 shows in a qualitative way the vastly superior resistance to dynamic oxidation at Mach 1 of Si_3N_4 compared to the Ni-based superalloy, TDNiCr (1). Such results encouraged us to embark on a number of ceramic programs. This paper will review some of the recent NASA supported work to improve silicon nitride based ceramics.

The goals of our work are threefold: (1) to improve the toughness of ceramics; (2) to improve their durability, i.e., their resistance to their working environment; and (3) to identify materials which can be fabricated to near net shape and high density by means other than conventional hot pressing and grinding. Of course, complex shapes can be machined from hot pressed billets of Si_3N_4 by diamond grinding. For example fig. 2 shows a turbine blade machined from hot pressed Si_3N_4 (2). However, it is desirable to seek lower cost ways of fabricating air foils.

The work to be discussed here is based on 4 NASA contracts one at AVCO, Systems Division, one at Norton Co., and two at United Technology Research Center (UTRC). It concerns improving the toughness and strength of hot pressed Si_3N_4 (HPSN), improving the strength and oxidation resistance of reaction sintered Si_3N_4 (RSSN), a material that can be slip cast or injection molded to size, and improving the strength and oxidation resistance of sinterable compositions of Si, Al, O, and N usually referred to as SiAlONs.

PART I

IMPROVED HOT PRESSED Si_3N_4

Despite our interest in materials that can be formed to shape by processes other than hot pressing we have also been interested in improving the toughness of the strongest forms of Si_3N_4 available, i.e., hot pressed Si_3N_4 . Hot pressed Si_3N_4 often contains MgO as an aid to densification. The MgO reacts with SiO_2 , which is on the surface of each particle of Si_3N_4 , to form a glass which on cooling from the pressing temperatures becomes Mg_2SiO_4 (enstatite). The resulting hot pressed material can be fully dense with a room temperature strength in 4 point bending of about 852 MN/m^2 (140 ksi). However, the strength falls off rapidly at about 1000° C (1830° F) (3) where enstatite begins to soften. Impurities can contribute to this softening and further reduce high temperature strength.

In work at AVCO the strength and toughness of HPSN were improved first by increasing the purity of the starting powder and second by using a more refractory additive or densification aid (4). The toughness was also increased and the scatter in properties reduced by air classifying the starting powder to remove powder particles greater than $10 \mu\text{m}$.

Silicon Nitride Powder

Advanced Materials Engineering Ltd. (AME) controlled phase grade (CP-85), a widely used silicon nitride powder, was used as a standard of comparison. It contained 0.25 weight percent Ca, an element that is detrimental to the high temperature strength of silicon nitride.

Special high purity silicon nitride powder with low Ca was also obtained from AME. Its Ca content ranged from 0.008 to 0.048 weight percent, factors of 30 to 5 times less than in the CP-85 powder. X-ray analysis of the powders showed the CP-85 to be 85 percent alpha and 15 percent beta. Alpha is the

preferred starting phase in hot pressing silicon nitride. The special powders ranged from 77 to 91 percent alpha.

Additives

To observe the effect of additives, MgO as well as other oxides were added to the controlled phase grade CP-85 powder and the high purity powders. These additives were selected to improve the elevated temperature properties of silicon nitride by achieving a more refractory grain boundary phase through reaction with the inherent SiO₂ impurity. The additives used were MgO, CaO, Y₂O₃, Al₂O₃, and ZrO₂ (stabilized with Y₂O₃). They were added on the assumption that they might form high melting point eutectics, which might be less detrimental to the high temperature properties of silicon nitride than the CaO-MgO-SiO₂ eutectic, which melts at 1336° C (2437° F). This ternary eutectic may form instead of the higher melting 1543° C (2809° F) MgO-SiO₂ eutectic when MgO is added to Ca containing silicon nitride. The powders mixed with the additives were hot pressed at 1750° C (3180° F) and 27.5 MN/m² (4000 psi) for 2 hours.

Strength and Impact Resistance

Figure 3 shows the effect on bend strength of 4 weight percent additions of the various additives to the reference powder CP-85. The addition of Y₂O₃ resulted in the highest strength at room temperature. The addition of ZrO₂ resulted in the highest strength at 1325° C (2920° F).

The higher purity powders resulted in improved short time bend strength as well as improved rupture strength and Charpy impact resistance. Greater powder purity and the use of a more refractory additive, ZrO₂, considerably increased the rupture life of Si₃N₄ bars. This is shown in fig. 4. Reducing Ca in the starting powder from 2500 to 400 ppm increased rupture life when MgO was the additive. Life was further increased when ZrO₂ instead of MgO was added to the low Ca powder.

In the AVCO study higher impact resistance paralleled higher bend strength. For example, a material with a 4 weight percent addition of ZrO₂ was stronger and also had greater impact resistance than material with a corresponding MgO addition. Their impact resistance is shown in fig. 5. The figure also shows that in addition to having greater resistance to impact, the material with 4 percent MgO. This is attributed to the air classification which was used to remove particles greater than 10 μm in the lot of powder to which the ZrO₂ was added, thus reducing the expected flaw size. The work just described is being pursued further to determine what level of ZrO₂ produces the best stress rupture and creep properties in hot pressed silicon nitride.

PART II

INCREASING TOUGHNESS OF SILICON NITRIDE

Another NASA program, performed by UTRC (United Technologies Research Center), has been aimed at increasing the toughness of fully dense silicon nitride by surface treatments (5). The effectiveness of the treatments was evaluated by instrumented Charpy impact tests and by ballistic impact tests from room temperature to 1370° C (2500° F). The base material used was NC-132 hot pressed silicon nitride made by Norton Co. (3). The treatments were carburizing to induce compressive surface stresses, and the application of energy absorbing layers (EAL). The energy absorbing layers were designed to be microcracked (such as zirconia, iron and magnesium titanate, and silica-zircon) or porous (reaction sintered Si₃N₄). Most of the EALs were cemented to the silicon nitride with a refractory cement, however some were formed or reacted in place.

Baseline NC-132

Control samples of NC-132 were tested at room temperature (RT), 1250° C (2280° F) and 1370° C (2500° F) in instrumented Charpy impact, a test which records both load and energy absorbed during the fracture process. The impact resistance of the Si₃N₄ which averaged 0.4 joules (3.5 in.-lb) at RT increased to 0.45 joules (4.0 in.-lb) at 1250° C (2280° F) and then returned to the RT value of 1370° C (2500° F). The maximum load to failure decreased gradually as temperature increased. It was 3.7 kN (840 lb) at RT but 2.8 kN (620 lb) at 1370° C (2500° F). A typical instrumented Charpy impact trace at RT is shown in fig. 6. The upper curve represents the energy absorbed, the lower curve the load. The horizontal axis is time.

Effect of Oxidation

Carburizing was found to be ineffective in increasing toughness in this study. However, some unexpected information was obtained in the course of the carburizing investigation. Reference samples were heated in air at 1350° C (2460° F) for 48 hours to see if heating without carburizing had an effect. The effect of an oxidized surface layer which formed on these samples was disastrous. The impact strength at RT dropped from 0.40 joules (3.5 in.-lb) for unoxidized to 0.14 joules (1.2 in.-lb) for oxidized specimens. The loss in strength was also verified in slow 3 point bend tests. Removal of about 10 μm (5 mils) from the tensile surface of oxidized bars partially restored their strength, but the oxidized sides of the test bars were weak enough to originate fracture. The loss of strength, as a result of oxidation, was attributed to the formation of silicates which created voids or pits on the surface and which acted as crack initiators.

A parallel set of experiments were performed with Si₃N₄ fabricated at UTRC with 15 weight percent Y₂O₃ instead of MgO as an additive. After 60 hours at 1350° C (2460° F) this material exhibited a drop in impact energy of only 22 percent compared to 68 percent for NC-132. Although the oxidized

UTRC Si_3N_4 + 15 percent Y_2O_3 had a generally rougher surface than the NC-132, it did not develop the large surface pits that NC-132 did. These pits were the origins of fracture in the oxidized NC-132. At one time it was assumed that ceramics including Si_3N_4 were immune to environmental effects. This is obviously not true, and much more work remains to be done to understand and design against environmental damage.

ENERGY ABSORBING LAYERS

Energy absorbing layers approximately 1 mm thick were cut from bulk samples of the EAL materials and cemented to the NC-132 Si_3N_4 substrate with a high temperature refractory cement.

Charpy Impact

ZrO₂. The ZrO_2 was partially stabilized with CaO. This material contained many microcracked grains because of the large internal stresses developed on transformation from tetragonal to monoclinic during cooling. Figure 7 shows the effect of this and other EALs on the room temperature, 1250° and 1370° C (2280° and 2500° F) impact energy. The tests were performed with the EAL on the impact side of the specimens. Although ZrO_2 layers did increase the impact resistance of the NC-132, the modest increase of 90 percent at RT was far below the 1.36 joules 12 in.-lb goal of the program.

Fe₂TiO₅. The greatest increase in Charpy impact resistance was achieved with iron titanate. While at RT the impact energy was only 0.69 joules (6.1 in.-lb), it was 2.56 joules (22.6 in.-lb) at 1250° C (2280° F) and 2.14 joules (18.9 in.-lb) at 1370° C (2500° F), well over the program goal of 1.36 joules (12 in.-lb). From the hump in the instrumented impact load versus time trace (see fig. 8) it is evident that a large amount of energy was absorbed with about half the total impact energy being due to the crushing of the iron titanate layer.

Silica-Zircon. The silica-zircon material (70 percent silica-30 percent zircon) was approximately 60 percent dense. It is a core material used for casting superalloys. This material increased the impact resistance three fold when cemented to the specimens. Impact resistance decreased as test temperature increased. This may have been due to an increase in the density of the EAL as a result of sintering. Heat treatments designed to vary the amount of microcracking in these EALs increased the energy absorbed in room temperature tests, even at low levels of microcracking.

Silica-Zircon-Mullite Slurry. EALs must eventually be applied to curved airfoil surfaces if they are to be of practical value. Therefore, another approach to applying them, dipping into a slurry, was tried. The slurry was similar to the silicon-zircon layers but contained in addition some mullite. The specimens were dipped repeatedly until a layer about 1 mm thick was formed. After dipping, some specimens were fired at 1000° C (1830° F) and some at 1200° C (2190° F). The layer fired at 1000° C (1830° F) was the more adherent

and resulted in the greater energy to break the specimens in room temperature tests. However, the slurry layers were not particularly effective and at most doubled the impact energy.

Reaction Sintered Silicon Nitride. It became evident in the Charpy testing and later in ballistic impact testing that the EALs were spalling as a result of impact. Thus, although they might protect the substrate from a single impact, they would be ineffective in protecting it against repeated impacts. Moreover, the EALs previously discussed had higher thermal coefficients of expansion than Si_3N_4 , and in addition to not surviving impact, did not survive thermal cycling. Therefore, a crushable layer was sought that would have a coefficient of expansion similar to the Si_3N_4 substrate. A low density reaction sintered Si_3N_4 was chosen. Instead of cementing this EAL on the surface of the NC-132 specimens, it was formed by reacting it in place. A slurry of silicon metal powder was applied in a 1 to 1.2 mm thick layer on one face of the Charpy specimens and ballistic impact specimens. The latter will be discussed in more detail later. After drying, the slurry was sintered for 16 hours at $1375^\circ\text{-}1400^\circ\text{ C}$ ($2510^\circ\text{-}2540^\circ\text{ F}$) in nitrogen. Two mesh sizes of silicon powder were used, -200 and -100/+200. The porosity of the -100/+200 material was about 40 percent while that of the -200 mesh material was about 30 percent. As fig. 7 shows the coarser -100/+200 mesh layer somewhat more than doubled the impact resistance of Si_3N_4 . The more dense -200 mesh layer had a negligible effect.

Ballistic Impact

Although the instrumented Charpy impact tests provide insight into how the EALs behave, ballistic impact tests more nearly simulate the hazards to be encountered in an engine. Ballistic impact specimens 2.54 cm x 3.81 cm x 6.4 mm were held in a vise with a 2.54 cm x 2.54 cm area projecting. Pellets of hardened steel 4.4 mm in diameter and weighing 0.37 g were fired at the center of the projecting square. An air rifle using helium pressure fired the pellets at the target. For the control specimens, the initial pressure was selected to provide a velocity of 150 m/sec (490 ft/sec). The pressure was then increased in 0.345 MN/m^2 (50 psi) increments, until the specimen broke. The fracture origin was almost always at the point of impact and due to Hertzian cracking. Figure 9 summarizes the effect of the EALs on the maximum energy absorbed without fracture of the Si_3N_4 substrate. At higher energies (velocities) the predominant mode of failure was by Hertzian cracking, but at the higher temperatures the mode of failure was about equally divided between Hertzian failure on the impact surface and tensile failure on the side of the specimen opposite the impact.

Although greater energy was absorbed by the iron titanate and the silica-zircon layers than by the RSSN layers, the RSSN is favored. Figure 10 shows the reason. The reaction sintered porous silicon nitride is more adherent than the other types of EALS. At high temperatures the RSSN survived impacts that caused other materials to spall.

This work is being continued at UTRC to improve the adherence and increase the energy absorbed. Other methods of introducing porosity are being

explored, e.g., the use of other mesh sizes and firing schedules is being studied. It has also been suggested that the surface of the RSSN layer be covered with a layer of CVD Si_3N_4 to protect it from oxidation.

Much remains to be done. The results to date, however, suggest that the energy absorbing layers have the potential for protecting the dense substrates from Hertzian cracks resulting from impact by small foreign objects. Such cracks could propagate under service stress to catastrophic proportions as the result of slow crack growth. Therefore, an EAL might well increase the engine life of dense ceramic turbine blades.

PART III

IMPROVED REACTION SINTERED SILICON NITRIDE

A third area in which NASA has supported research in silicon nitride-based ceramics is in the improvement of the strength and oxidation resistance of reaction sintered silicon nitride. This work was done by the Norton Co. (6).

Reaction sintered silicon nitride, (RSSN), is made by nitriding silicon metal powders (7). The powder is first formed to a shape by one of several methods such as slip casting, cold pressing, or injection molding. The shaped object is heated to drive off any binder that is used to give it green strength. It is sometimes sintered in argon to make it strong enough to handle while performing prenitriding machining operations. Finally, it is heated in an atmosphere of nitrogen. The nitrogen reacts with the silicon metal to form Si_3N_4 . This step is called reaction sintering. The initial silicon compact usually has a density of about 1.4-1.7 g/cm^3 . It gains weight during its reaction with nitrogen as Si_3N_4 grows in the voids between Si particles, but contrary to most sintering operations, it does not shrink. Because nitrogen must have access to the unreacted silicon for the sintering to occur, it is not possible to make fully dense RSSN. A typical commercial product has a density of 2.2 to 2.4 g/cm^3 compared to a theoretical density of 3.2 g/cm^3 for Si_3N_4 . As a consequence of its porosity, RSSN has much lower room temperature strength than hot pressed Si_3N_4 . However, because RSSN can be made without the densifying or sintering additives required for hot pressed Si_3N_4 (HPSN), it has superior strength at high temperature. The additives which permit densifying of the HPSN also make it subject to creep at high temperatures. Despite its porosity then, RSSN has greater creep strength at high temperatures (>1370° C (2500° F)) than hot pressed Si_3N_4 .

Unfortunately, the porosity of RSSN results in poor oxidation resistance as well as low room temperature strength. For example, two-thirds of the initial strength of RSSN can be lost as the result of exposure in the 1200°-1300° C (2190°-2370° F). A major reason for the loss of strength after oxidation is the formation of cristobalite (SiO_2) during oxidation. Cristobalite undergoes a phase transformation to tridymite upon cooling. The large volume expansion accompanying this transformation produces cracks in the oxidation product which can initiate fracture in the RSSN.

Surface Treatments

Since the as-nitrided strength of better quality RSSN is controlled by surface flaws, and since oxidation is a surface-related phenomena, it was believed that surface treatments to the RSSN to densify the surface might simultaneously reduce surface flaw severity and form an oxidation barrier.

The principal criteria for evaluating a given treatment were: (1) the post-treatment strength and, (2) the strength of treated specimens after a 12-hour air oxidation at 1250° C (2280° F). The most successful method of densifying the RSSN surface was impregnation with liquid solutions. The use of solutions permits penetration of internal porosity. In addition, having been derived from solutions, the reactants are finely divided, capable of being intimately mixed, and more reactive.

Solutions which would yield both mixed and single oxides upon heating were investigated. Solutions were generally forced into the RSSN bars under isostatic pressure. After impregnation, excess solvents were evaporated and the solutes were decomposed to oxides by slow heating in air at temperatures up to about 700° C (1290° F). The specimens were then fired under nitrogen at an elevated temperature to complete the treatment.

Mixed Oxides. Solutions which would lead to the formation of either mullite, zircon, enstatite, or spinel were investigated. These solids were selected as pore fillers on the basis of their high temperature stability, oxidation resistance, relatively low, and therefore close to matching, thermal expansion coefficients, and expected compatibility with silicon nitride.

Although some individual strengths, measured after firing at the lower temperatures, were significantly in excess of the untreated baseline strength, improvements were not always observed. Therefore, work with the mixed oxides was abandoned when single oxides showed more promise for strengthening.

Single Oxides. Single oxides significantly increase strength. Most of this work involved the oxides alumina and zirconia, although others were briefly studied. The primary means of introducing the oxides into the RSSN was isostatic impregnation with solutions which were then thermally decomposed to an oxide in air before high temperature firing. For alumina, aluminum nitrate in ethyl alcohol was used, while for zirconia, zirconyl chloride in water was used. Samples were fired between 1200° and 1740° C (2190° and 3160° F) for 2-8 hours in a predominately nitrogen atmosphere. When the atmosphere also contained silicon monoxide generated from a powder mixture of silicon and silica the greatest increases in strength occurred. The SiO containing atmosphere may have prevented decomposition of Si₃N₄.

Strength and Structure

Room temperature 4 point bend strengths for several firing conditions between 1350° and 1500° C (2460° and 2730° F) are shown in Table I. Individual bend strengths in excess of 434 MN/m² (63 ksi) were recorded and mean strengths of treated groups exceeded the as-nitrided strength by up to 45 percent.

Higher temperature firings (2 hr at each of 1550°, 1650°, and 1740° C (2820°, 3000°, and 3160° F)) of impregnated samples showed no strength increase and frequently strength losses.

Scanning electron microscopy and electron probe examination showed that material modifications were restricted to a very thin surface layer, which in some cases, was densified by the processing. This is consistent with the concept that the strength of as-nitrided RSSN is surface flaw controlled and that the improved strength was due to a beneficial modification of these surface flaws.

Oxidation Resistance

Impregnation of the surface of RSSN to seal its pores was considered as a way to improve oxidation resistance as well as to increase strength. Resistance to oxidation, or perhaps more properly resistance to oxidation damage, was evaluated by comparing the strength of treated and untreated RSSN after isothermal oxidation in air for 12 hours at 1250° C (2190° F). This is a temperature found to be especially detrimental to the strength of RSSN. Table II summarizes observations on the oxidation behavior of RSSN with a baseline strength of 290 MN/m² (42 ksi) impregnated with Al(NO₃)₃ and ZrOCl₂. Although no treatment retained the as-nitrided strength, the loss of strength was substantially reduced. For example, the oxidation exposure reduced the strength of the untreated material 60 percent. Impregnation with Al(NO₃)₃ and firing for 16 hours at 1400° C (2500° F) in an atmosphere of N₂ and SiO limited the reduction in strength after oxidation to only 14 percent.

Improved Baseline Material

During the course of this program the Norton Co. improved their nitriding procedures. As a result the baseline strength of as nitrided RSSN was increased from 290 MN/m² (42 ksi) to 353 MN/m² (51 ksi). This improved baseline material was given the same impregnating treatments as were used for the weaker baseline material with two exceptions. First in addition to an impregnation that produced ZrO₂, a solution containing yttrium nitrate along with zirconyl chloride was used. It gave a Y₂O₃/ZrO₂ ratio of 0.08 intended to stabilize the ZrO₂. Second, the three systems, Al₂O₃, ZrO₂, and ZrO₂ + Y₂O₃ were all fired in an N₂/SiO atmosphere at 1500° C (2730° F) after impregnation. The results were particularly encouraging as can be seen in table III. Although the as fired strength of this impregnated material was somewhat less than its initial as nitrided strength, the post oxidation (12 hr at 1250° C (2280° F)) strengths were among the highest yet observed after such exposure. In one instance, for the ZrO₂ + Y₂O₃ impregnation, the strength after oxidation at 1250° C (2280° F) actually was greater than the as fired strength, although less than as nitrided.

The results in this program have been difficult to reproduce, but the high values of strength have been encouraging. RSSN is such an attractive material because of its ease of molding to shape and because of its high creep strength at high temperatures that impregnation or other methods of improving

its durability should be pursued.

PART IV

SiALON

The final program to be discussed was devoted to improving the strength and, incidentally, the oxidation resistance of SiALON. This work was done at United Technology Research Center (UTRC) (8). "SiALON" is used to describe ceramics based on the elements Si, Al, O, and N. The early SiALONs were made by high temperature reactions between Si_3N_4 and Al_2O_3 (9, 10). The SiALONs were reported to have good thermal shock resistance, low coefficient of thermal expansion, good high temperature rupture modulus, good high temperature creep resistance, and good oxidation resistance.

It was initially believed that mixtures of Si_3N_4 and up to about 70 weight percent Al_2O_3 could be sintered to high density as solid solutions having a β' expanded Si_3N_4 structure. Recent phase equilibrium studies (9, 10) have shown that the β' solid solution homogeneity range lies not between Si_3N_4 and Al_2O_3 , but between Si_3N_4 and a composition approximately $\text{SiAl}_2\text{O}_2\text{N}_2$. Mixtures of Al_2O_3 and Si_3N_4 sinter to a multiphase structure. A tentative diagram (fig. 11) of the quaternary system Si_3N_4 -AlN-SiO₂- Al_2O_3 which was developed in a parallel program (10) was used to select those compositions studied and which is described in detail in reference 9. Composition can be expressed as $\text{Si}_3\text{-Al}_x\text{O}_x\text{N}_{4-x}$ where Al and O are substituted for Si and N in Si_3N_4 in the amount x.

The objective of the program was to develop a process for pressureless sintering high density, high strength, single phase β' SiALON with potential for use in gas turbine engines. It is now known that pure β' solid solutions have little propensity for sintering. The sinterability of Si_3N_4 - Al_2O_3 mixtures is strongly dependent on the presence of low melting (<1800° C) (3270° F) phases. Therefore, the approach was to add sintering aids to a mixture of Si_3N_4 , AlN, and Al_2O_3 that would form a β' solid solution. The sintering aids investigated were selected from compounds that have been shown to be effective in the densification of Si_3N_4 by hot pressing.

Materials and Specimen Preparation

Materials used for compounding the basic β' SiALON compositions were: 90% $\alpha\text{Si}_3\text{N}_4$ -300 mesh powder, and 99.9%-325 mesh AlN, and Al_2O_3 . Compounds added to basic β' compositions to promote sintering were CeO_2 , Y_2O_3 , ZrO_2 , AlPO_4 , GaPO_4 , HfO_2 , and Cr_2O_3 .

The compositions of the basic β' SiALON solid solutions most extensively investigated are listed in atom percent in table IV and are plotted on fig. 11. The numerals 0.30 through 1.60 which locate the compositions on the figure are the values of x in the formula $\text{Si}_{3-x}\text{Al}_x\text{O}_x\text{N}_{4-x}$.

The basic β' composition made from Si_3N_4 , Al_2O_3 , and AlN was blended

with the additives. It was then ball milled 96 hours in a polyethylene mill with Al_2O_3 grinding media. The mill charge was dried rapidly by spraying it from a wash bottle onto a heated aluminum plate. The charge was then heated in air to 600°C (1100°F) to burn out polyethylene contamination.

The prepared powder was pressed in a rectangular steel mold. The resulting bars were then hydrostatically pressed at 276 MN/m^2 (40 ksi) in plastic bags. They were heated in air to 600°C (1100°F) and, then they were sintered in nitrogen in a closed boron nitride crucible at temperatures from 1650°C – 1800°C (3000°F – 3270°F).

Sample Characteristics

Samples were characterized by density and porosity measurements, metallography, and X-ray diffraction. Flexural strength was measured in 4-point bending. Most testing was at room temperature but some tests were performed at 1370°C (2500°F). Selected fracture surfaces were examined in the scanning electron microscope. Static air oxidation testing was carried out on selected specimens at 1000°C (1830°F) and at 1400°C (2550°C). The samples were removed from the furnace periodically and weighed.

Structure and Properties

The effect of sintering aids on the apparent porosity of the SiAlON where $x = 0.55$ is shown in table V. Additions of CeO_2 , Y_2O_3 , and for the most part ZrO_2 resulted in zero apparent porosity. Additions of AlPO_4 , GaPO_4 , HfO_2 , and Cr_2O_3 were ineffective as sintering aids, producing bars with a porosity of about 20 percent. As a consequence, the materials that were most studied were made with the more effective sintering aids CeO_2 , Y_2O_3 , or ZrO_2 .

Microstructural and Mechanical Test Data

The most complete data were obtained on the β' SiAlONs densified by the addition of CeO_2 . When they were etched with HF , the microstructures showed predominantly acicular β' grains embedded in a matrix phase or phases which were deeply etched. X-ray data indicated that the matrix phase changed composition from an unidentified phase where $x = 0.55$ to a phase apparently isomorphous with $\text{SiO}_2 \cdot 4\text{AlN}$ where $x = 1.6$. The micrographs, fig. 12, indicate a coarsening of the microstructure in going along the β' line from where $x = 0.55$, low in Al_2O_3 , to where $x = 1.60$, high in Al_2O_3 .

Strength and density as functions of Al content for 3 different SiAlONs each with 10 w/o CeO_2 and prepared under similar conditions are presented in Fig. 13. Both show decreases with increasing aluminum (and oxygen) substitution for silicon (nitrogen). Whether the strength decrease was related to the coarsening of the microstructure, the change in matrix phase, the lowering of the density or to still another cause could not be determined from the data at hand. However, the results suggested that attention should be concentrated on the high Si_3N_4 end of the β' composition line.

Figure 14 summarizes strength results at room temperature and at 1370° C (2500° F) for two β' compositions ($x = 0.55$ and $x = 0.30$). Maximum room temperature strengths in the neighborhood of 550 MN/m² (80 ksi) were obtained with both β' SiAlONs and with additives of CeO₂, Y₂O₃, or ZrO₂.

The large scatter in strength in some compositions may have been due to agglomerates or inclusions that can be sources of stress concentration. The micrographs in Figs. 15 and 16 show large grains or voids, near the surfaces of the specimens, which are associated with the initiation of fracture.

At 1370° C (2500° F), the greatest strength obtained was 462 MN/m² (67 ksi) for composition ($x = 0.30$) + 2.5% Y₂O₃. Although little high temperature testing had been completed at this writing, the results with ZrO₂ bearing compositions were not encouraging. Whereas the creep rate of ($x = 0.55$) + 5% Y₂O₃ was 6×10^{-5} hr⁻¹ at 1370° C (2500° F) and 10 ksi, it was 2×10^{-3} hr⁻¹ or 300 times greater for ($x = 0.55$) + 5 w/o (0.8 ZrO₂ + 0.2 Y₂O₃). The creep rate for the 5 w/o Y₂O₃ material is better, being comparable to that (10×10^{-5} hr⁻¹) found for an early hot pressed silicon nitride, HS-130.

Oxidation Behavior

Figure 17 shows parabolic plots of typical oxidation behavior at 1400° C (2550° F). The material with CeO₂ additive had the highest weight gain. Material with ZrO₂ as its additive had the lowest oxidation rate. Unfortunately, the oxidation of the material with just ZrO₂ added was catastrophic at 1000° C (1830° F). This condition was attributed to the phase transformation of ZrO₂ from tetragonal to monoclinic. By adding a small proportion of Y₂O₃ to stabilize the ZrO₂, the catastrophic oxidation at 1000° C (1830° F) was eliminated.

To sum up the work on SiAlONs, this sinterable material which can be fabricated to shape has been shown to be capable of achieving bend strengths of 462 MN/m² (67 ksi) at 1370° C (2500° F) and to exhibit creep rates less than that of a fully dense hot pressed silicon nitride. Compositions have been developed that have good oxidation resistance. Unfortunately, this program has not yet developed a composition that combines in a single material both advantages.

CONCLUDING REMARKS

I have discussed four NASA-supported programs aimed at improving the properties of silicon nitride-based ceramics. I shall list the highlights of each program in the order in which I have presented them:

1. The use of a high purity Si₃N₄ starting powder with low calcium content and a more refractory sintering aid (ZrO₂ instead of MgO) improved room temperature and high temperature flexure strength of hot pressed silicon nitride. This approach also improved rupture strength and Charpy impact resistance.

2. Crushable energy absorbing layers (EAL) increased the resistance to

impact of a hot pressed silicon nitride, NC-132. The most promising approach was the use of a porous layer of reaction sintered silicon nitride, sintered in place. This material was the most adherent under both impact and thermal cycling.

3. Impregnation of reaction sintered silicon nitride (RSSN) with solutions that were then oxidized to Al_2O_3 or ZrO_2 increased bend strength at room temperature. These surface treatments also limited the degradation in strength experienced by untreated RSSN after oxidation at $1250^\circ C$ ($2280^\circ F$).

4. SiAlONs, compounds of Si, Al, O, and N with a β' (expanded Si_3N_4) structure, were sintered to full density through the use of sintering aids. The compounds CeO_2 , Y_2O_3 , and ZrO_2 were the most effective. Additions of Y_2O_3 provided the greatest strength. Additions of ZrO_2 provided the greatest oxidation resistance.

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Table I. Effect of Impregnation on Room Temperature 4 Point Bend Strength of RSSN Fired in N₂/SiO After Impregnation (6)

Impregnation system	Firing parameters		Post-treatment mean strength, MN/m ² (ksi)	Percent strength improvement
	Temperature, °C (°F)	Time, hr		
As-nitrided	-----	--	290 (42.1)	--
ZrOCl ₂ in water	1350 (2460)	3	368 (53.4)	27
ZrOCl ₂ in water	1500 (2730)	2	384 (55.7)	32
Al(NO ₃) ₂ in alcohol	1400 (2550)	3	421 (61.1)	45

Table II. Effect of Impregnation On As Fired and On Post Oxidation Strength at Room Temperature of RSSN Fired In N₂/SiO At 1400° C (2550° F) After Impregnation (6)

Impregnation system	Firing time, hr	Mean fired strength, MN/m ² (ksi)	Mean post 1250° C (2280° F) oxidation strength, MN/m ² (ksi)	Strength change ^b by oxidation, percent
Untreated ^a	--	290 (42.1)	117 (17.0)	-60
Al(NO ₃) ₃	3	318 (46.1)	166 (24.1)	-43
Al(NO ₃) ₃	3	302 (43.8)	166 (24.1)	-43
ZrOCl ₂	3	303 (43.9)	180 (26.1)	-34
Al(NO ₃) ₃	16	Not measured	250 (36.3)	-14
ZrOCl ₂	16	Not measured	160 (23.2)	-45

^a As nitrided.

$$^b 1 - \left(\frac{\text{Post oxidation strength}}{290} \right) \times 100.$$

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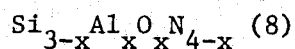
Table III. Effect of Impregnation on as Fired and Post Oxidation Strength of Improved Baseline RSSN Fired in N₂/SiO at 1500° C (2730° C) After Impregnation (6)

Impregnating system	Firing time, hr	Mean fired strength		Post oxidation ^a strength		Strength change ^b , percent
		MN/m ²	ksi	MN/m ²	ksi	
Untreated (as nitrided)	--	353	51.2	203	29.5	-42.3
Al(NO ₃) ₃	2	327	47	234	34	-33.6
Al(NO ₃) ₃	8	308	45	230	33	-35.5
ZrOCl ₂	2	326	47	293	43	-16
ZrOCl ₂	2	311	45	255	37	-27.7
+ Y(NO ₃) ₃						
ZrOCl ₂	8	349	36	318	46	-10.2
+ Y(NO ₃) ₃						

^aAir oxidation 12 hr at 1250° C (2280° F).

^b₁ - $\left(\frac{\text{Post oxidation strength}}{353} \right) \times 100.$

Table IV. Compositions of Basic Beta Prime Formula



x	Atom percent			
	Si	Al	O	N
1.60	20	22.86	22.86	34.28
1.07	27.50	15.36	15.36	41.78
.55	35	7.86	7.86	49.28
.30	37.57	4.29	4.29	52.86

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Table V. Effect of Sintering Aids on Density of

Basic Beta Prime $\text{Si}_{3-0.55}^{\text{Al}_{0.55}\text{O}_{0.55}\text{N}_{4-0.55}}$ (8)

Sintering aid		Sintering temperature		Apparent porosity
Name	W/O	°C	°F	
CeO ₂	2.5-1.0	1700-1785	3090-3245	0
Y ₂ O ₃	5-10	1750	3180	0
ZrO ₂	5-20	1700	3090	0
ZrO ₂	5	1650	3000	4.5
AlPO ₄	5	1735	3155	19
GaPO ₄	5	1735	3155	18
HfO ₂	8	1700-1800	3090-3270	20.22-22.75
Cr ₂ O ₃	2	1690-1735	3075-3155	20.95-24.52



NORTON (HS-130)
HOT PRESSED Si_3N_4
NO DAMAGE FOUND
 $\Delta\text{Wt} - 0.50 \text{ MG/CM}^2$



COMMERCIALY
COATED TD NiCr
 $\Delta\text{Wt} - 41.5 \text{ MG/CM}^2$
CS-68523

Fig. 1. - Ceramic and coated blades after 100 cycles in Mach 1 burner at 1200°C (1).

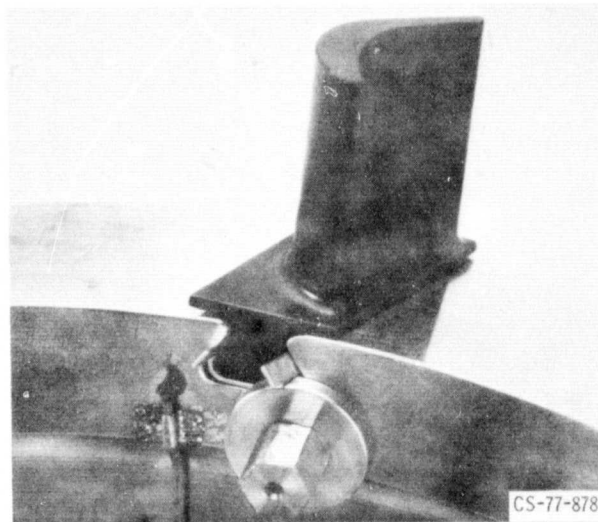


Fig. 2. - Diamond machined hot pressed silicon nitride turbine blade mounted in alloy disk for hot spin test (2).

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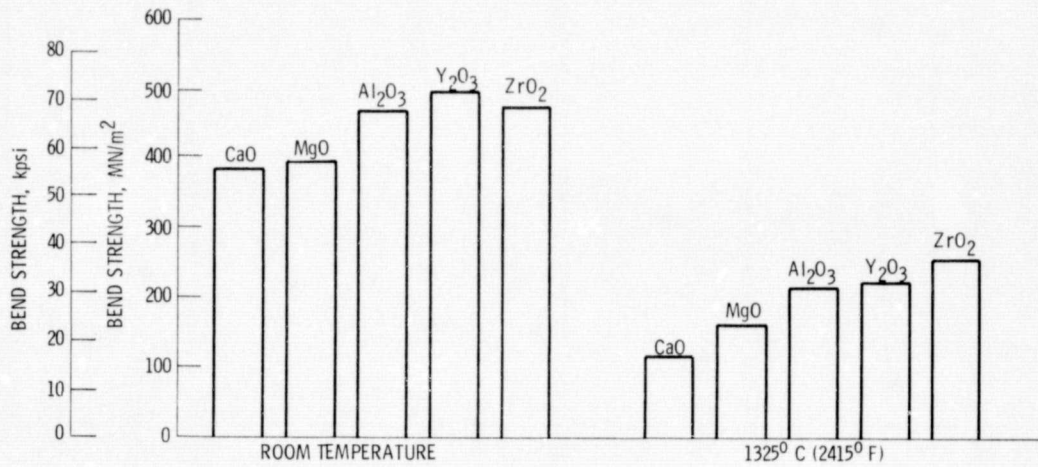


Fig. 3. Room temperature and 1325° C (2415° F) bend strength comparison for 4 w/o additions of various additives to AME controlled phase grade CP 85 Si₃N₄ powder (4).

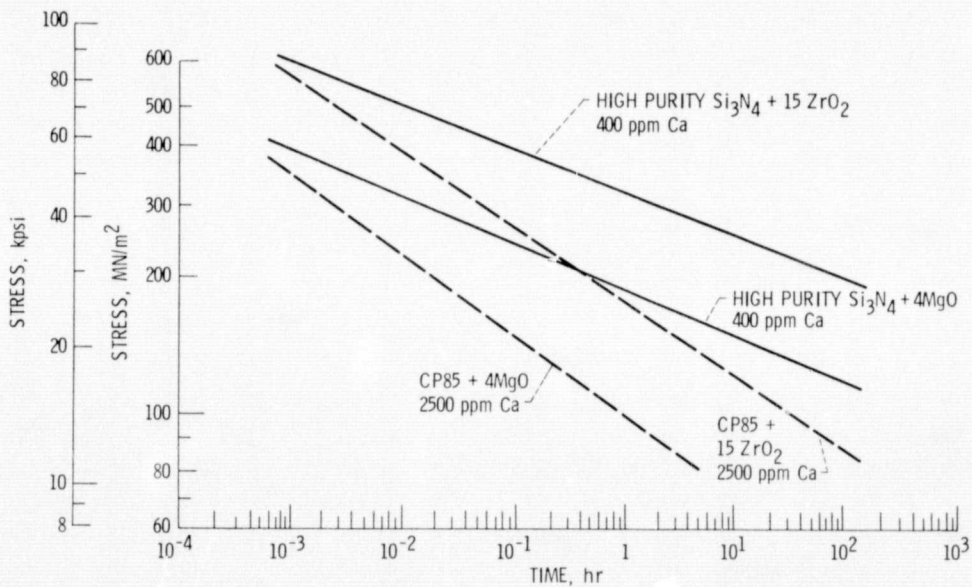


Fig. 4. Effect of starting powder purity and additives on 1325° C (2415° F) rupture properties of HPSN (4).

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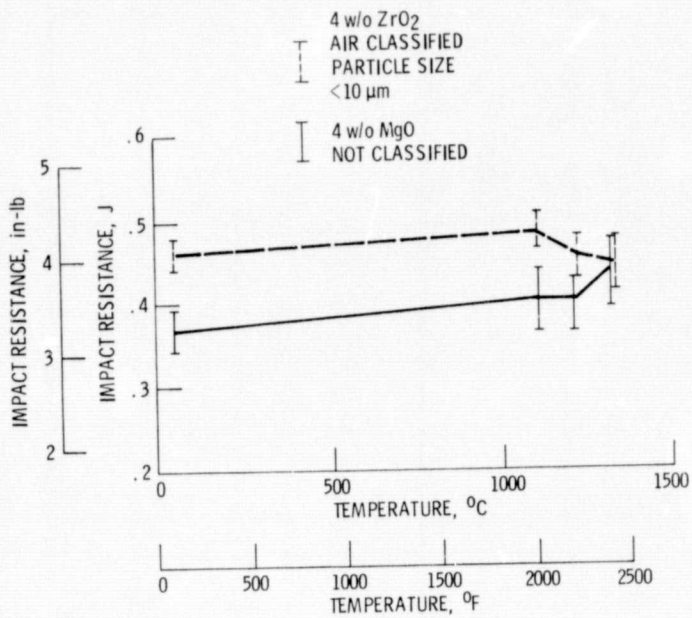


Fig. 5. Effect of powder classification and additives on Charpy impact resistance of high purity Si_3N_4 powder (4).

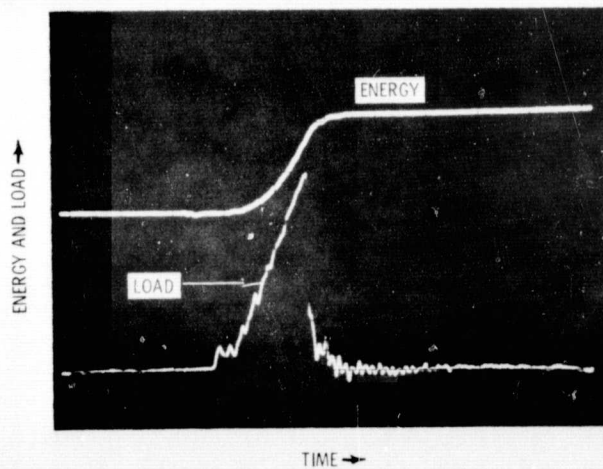


Fig. 6. - Instrumented Charpy impact test of NC-132 Si_3N_4 , as ground (5).

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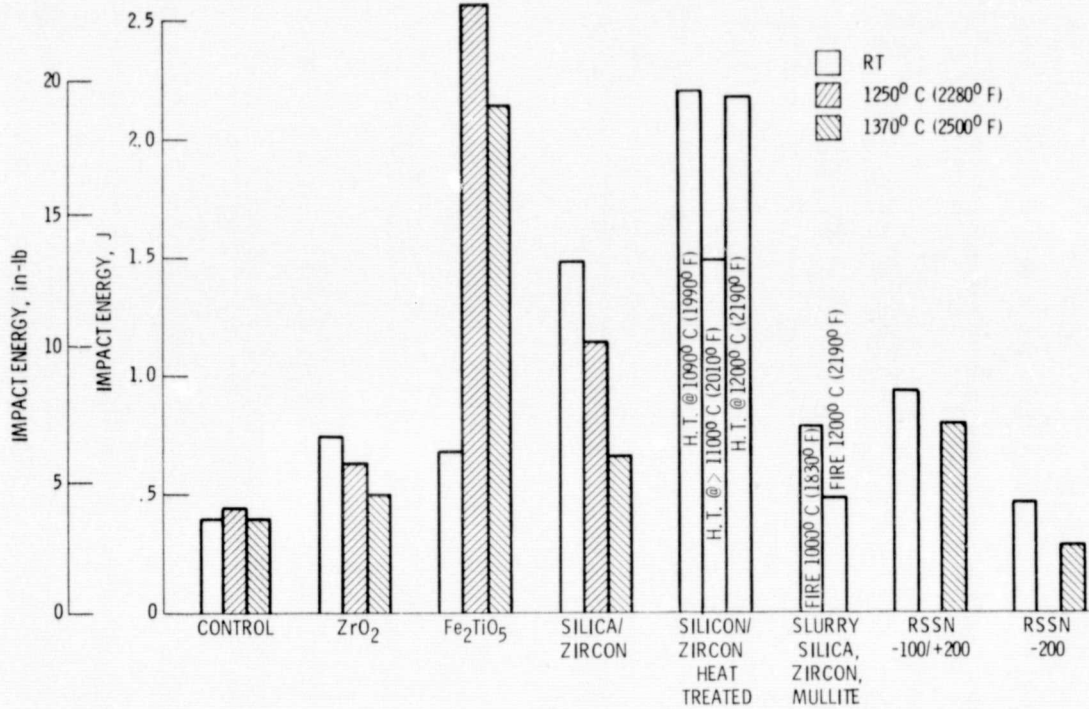


Fig. 7. Effect of energy absorbing layers on Charpy impact resistance (5).

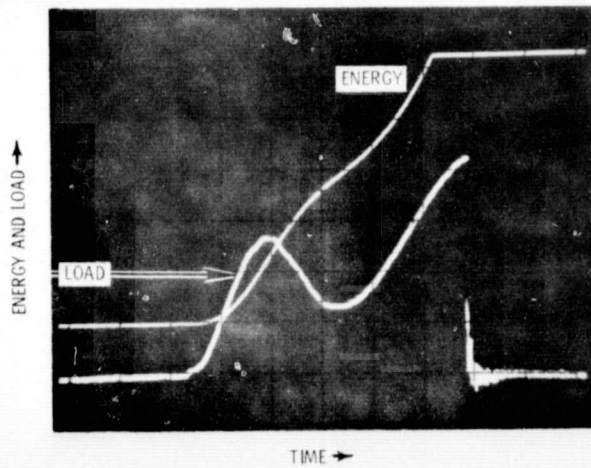


Fig. 8. -135°C (2460°F) instrumented Charpy impact test of Fe₂TiO₅ layer on Si₃N₄ (5).

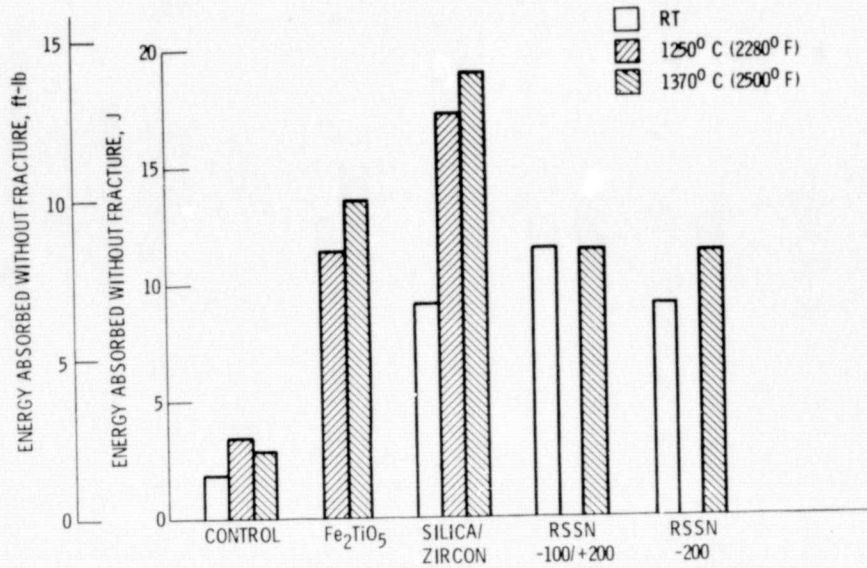
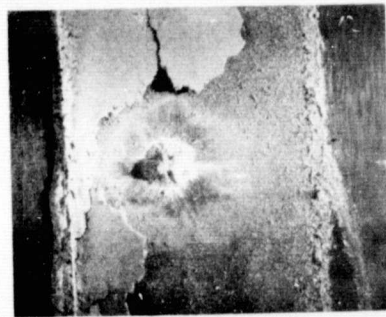
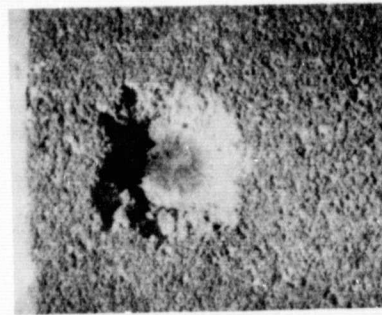


Fig. 9. Effect of energy absorbing layers on ballistic impact resistance (5).



IRON TITANATE EAL
1250°C (2280°F)
7.1 JOULES (5.2 ft-lb)



POROUS RSSN EAL
1370°C (2500°F)
9.1 JOULES (6.7 ft-lb)

BASE-LINE VALUE WITHOUT EAL 2.7 JOULES ≈(2 ft-lb)
FRACTURE OF SUBSTRATE OCCURS AT 12.3 JOULES ≈(9 ft-lb) CS-77-879

Fig. 10. - Si₃N₄ specimens with energy absorbing surface layers after ballistic impact (5).

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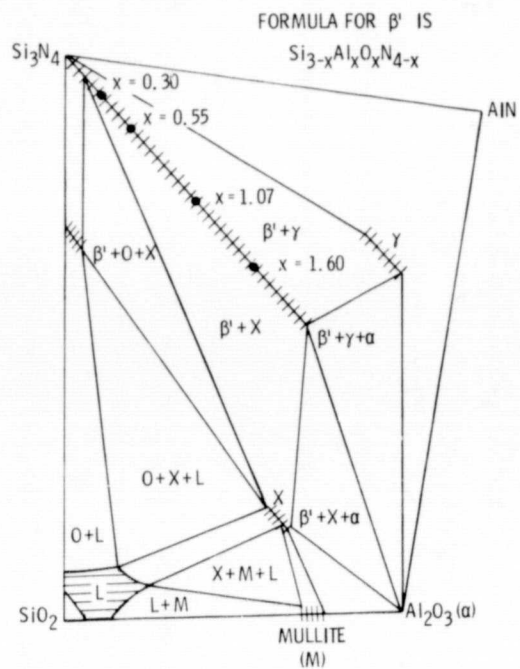


Fig. 11. System Si_3N_4 - AlN - Al_2O_3 - SiO_2 1650° C isothermal section (8).

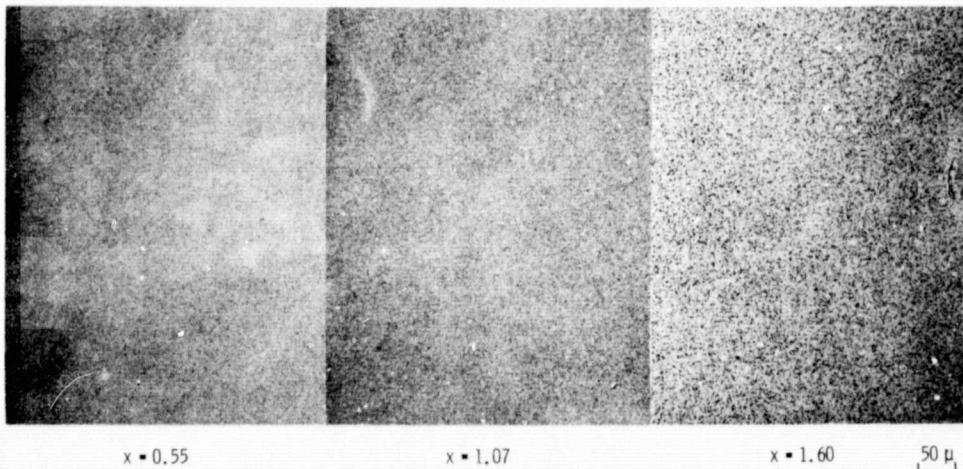


Fig. 12. - The effect of composition on the microstructure of $\text{Si}_{3-x}\text{Al}_x\text{O}_x\text{N}_{4-x}$ plus 10 weight percent CeO_2 (8).

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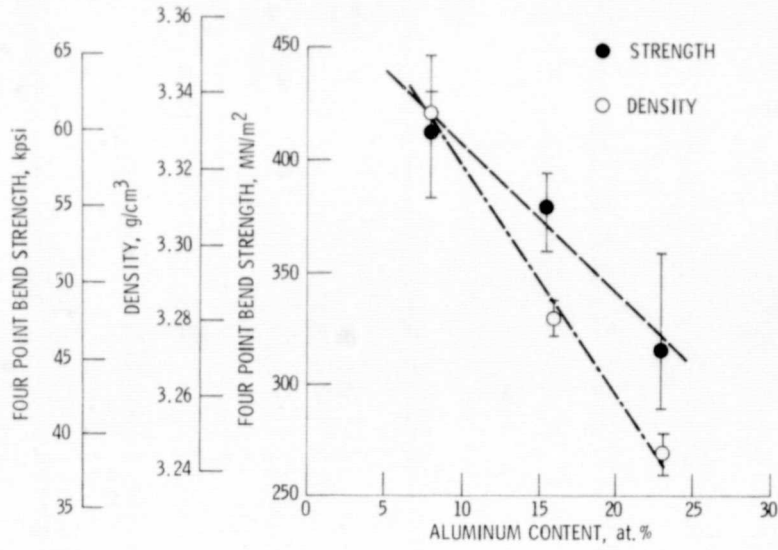


Fig. 13. Strength and density variation of β' + 10 w/o CeO_2 samples with Al content (8).

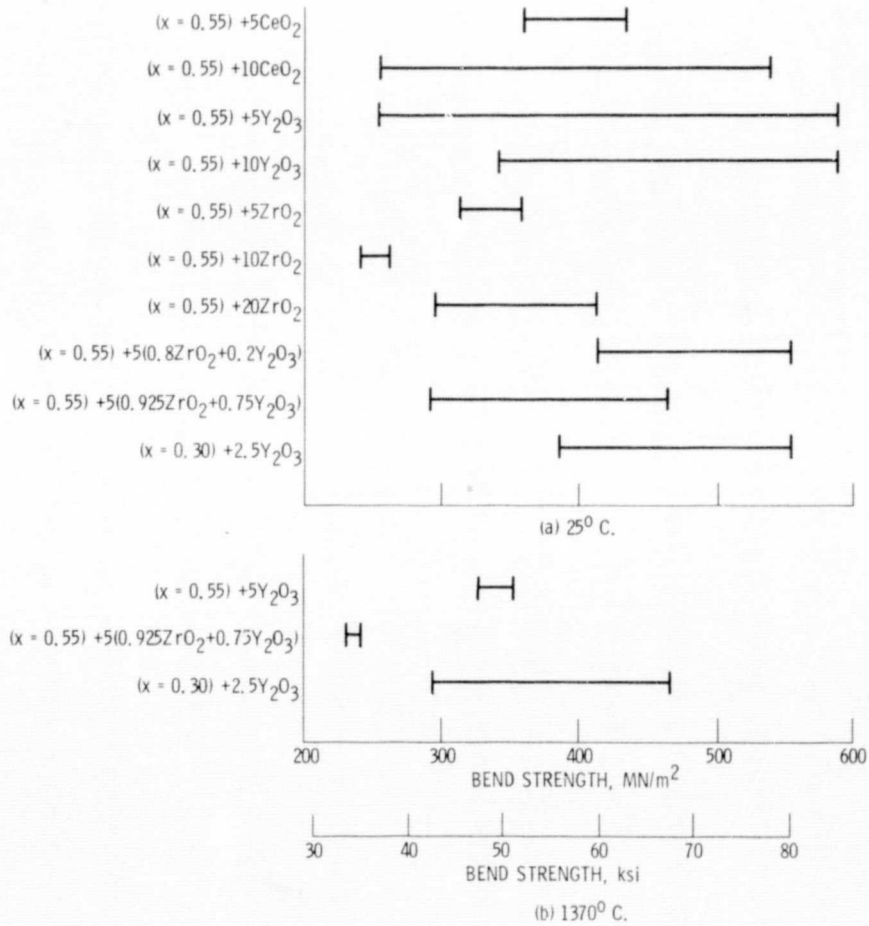


Fig. 14. Four point bend strength of SiAlON with various additives (8).

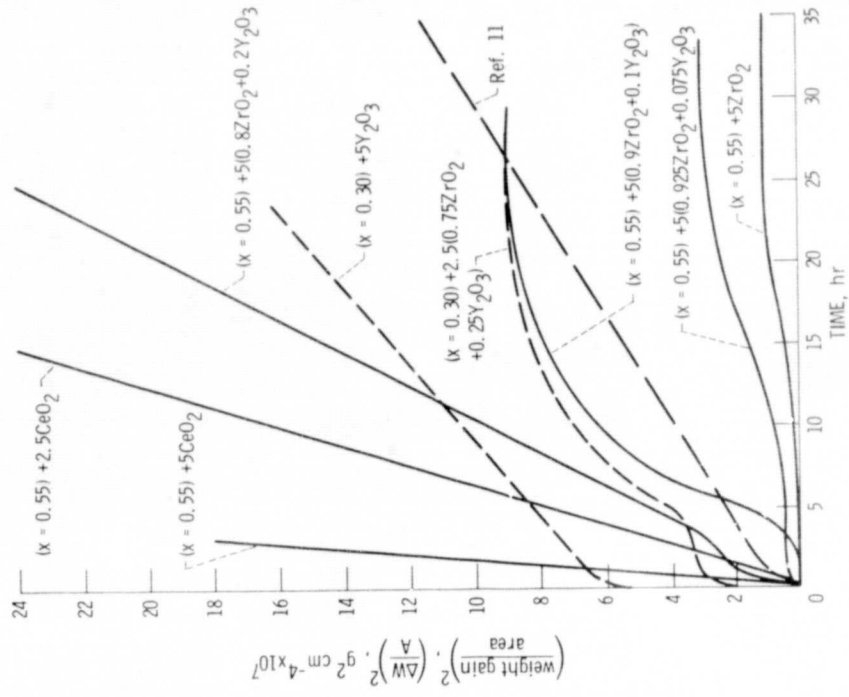


Fig. 17. Weight gain in air at 1400°C (2550°F) of various SIALON compositions ($Si_3-xAl_xO_5N_4-x$) (8).

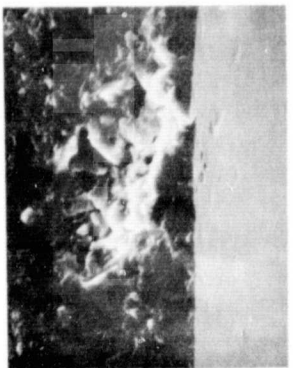


Fig. 15. - Fracture surface of SIALON composition ($x = 0.55$) $5 Y_2O_3$. Fracture initiated at void associated with large grains near tensile face; $\sigma = 510 \text{ MN/m}^2$ (74 ksi) (8).

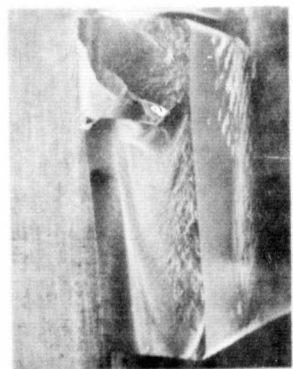


Fig. 16. - Fracture surface of SIALON composition ($x = 0.30$) $2.5Y_2O_3$. Fracture initiated at large grains or inclusion near tensile face; $\sigma = 386 \text{ MN/m}^2$ (56 ksi) (8).

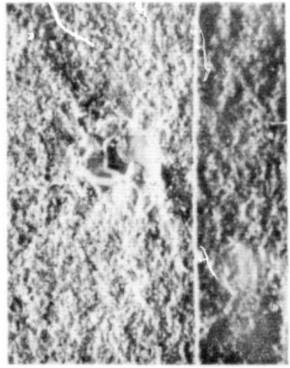


Fig. 16. - Fracture surface of SIALON composition ($x = 0.30$) $2.5Y_2O_3$. Fracture initiated at large grains or inclusion near tensile face; $\sigma = 386 \text{ MN/m}^2$ (56 ksi) (8).



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