NASA Technical Paper 1490



# Modulus of Rupture and Oxidation Resistance of $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$ Sialon

Alan Arias

JULY 1979

NASA

NASA Technical Paper 1490

# Modulus of Rupture and Oxidation Resistance of $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$ Sialon

Alan Arias
*Lewis Research Center*
*Cleveland, Ohio*

National Aeronautics
and Space Administration

**Scientific and Technical
Information Branch**

1979

## SUMMARY

The present investigation was undertaken to determine the modulus of rupture (MOR) as a function of temperature and the oxidation resistance of a Sialon without sintering aids, having the formula $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$, and with a molar oxygen-nitrogen ratio of 0.204. In this report, this Sialon composition is designated Sialon C.

The average MOR of Sialon C ranged from 404 megapascals (58.6 ksi) at room temperature to 254 megapascals (36.8 ksi) at 1400° C. These strength levels are better than those of other well-defined Sialons without sintering aids reported in the literature. The large scatter in the high-temperature MOR values, the relatively slow decrease in MOR with temperature, and the fact that in all tests the load-deflection curves to fracture were linear suggest that this Sialon may have better creep resistance than Sialons with $Y_2O_3$ or other additions.

Oxidation tests of Sialon C at 1400° C in air showed it to have excellent oxidation resistance. The parabolic oxidation rate constant for this Sialon at 1400° C is $2.5\times10^{-10}$ $g^2/cm^4$ hr and is the smallest value for a $Si_3N_4$-base ceramic reported in the literature.

Cyclic oxidation tests of Sialon C at 1400° C yielded a plot of weight gain as a function of time almost identical to that of the uncycled Sialon and a parabolic oxidation rate constant $\leq 2.8\times10^{-10}$ $g^2/cm^4$ hr. These results, the smoothness of the plots, and the fact that no debris of any kind was found in the platinum crucible in which the Sialon was oxidized indicate that no spalling occurred in 200 hours of oxidation.


## INTRODUCTION

In a previous investigation at the Lewis Research Center (ref. 1), it was shown that pressureless sintered Sialons could be made without additives by adjusting their oxygen-nitrogen ratio (O/N) to a value slightly in excess of the O/N for a $\beta'$-Sialon. The resulting Sialon sintered to better than 97 percent of its theoretical density and appeared to be essentially single-phase $\beta'$-Sialon, both by X-ray diffraction and by optical microscopy. The present investigation is a continuation of the program of reference 1, and its main objectives are to determine the modulus of rupture (MOR) and the oxidation resistance of a Sialon having the formula $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$. The composition of the Sialon is also indicated in the behavior diagram for the $Si_3N_4$-AlN-$Al_2O_3$-$SiO_2$ system (ref. 2) shown in figure 1. This Sialon is identical to Sialon C in reference 1 and is so designated in this report.

To carry out the objectives of the present investigation, Sialon C was compounded from separately milled $\alpha$-silicon nitride ($\alpha$-$Si_3N_4$), aluminum nitride (AlN), and silica ($SiO_2$). Cold-pressed bars of this composition were sintered in stagnant nitrogen. The sintered bars were used to determine the MOR as a function of temperature and the oxidation resistance at 1400° C.

## MATERIALS

The materials used in this investigation were powdered $\alpha$-$Si_3N_4$, AlN, and $SiO_2$. These materials are characterized in table I.

## EQUIPMENT

The equipment used in this investigation has been described in reference 3. Briefly, it consisted of 1.5-liter nickel-lined ball mills with nickel shot as grinding media; 1.4-liter alumina ball mills with alumina balls as grinding media; and standard laboratory equipment (presses, dies, furnaces, analytical equipment, etc.).

## PROCEDURES

The procedures used for the preparation and testing of Sialon C specimens are outlined in the flow diagram of figure 2. These procedures are described briefly in this section.

### Milling

The $\alpha$-$Si_3N_4$ and the $SiO_2$ were separately milled with water as the milling fluid in the nickel-lined mills for 300 and 130 hours, respectively. Most of the nickel powder resulting from the wear of balls and mills (pickup) was removed magnetically. The slurries were then treated with reagent grade concentrated nitric acid to dissolve the residual pickup. The powders were separated from the slurries by centrifuging. After being washed with water and centrifuged again, the powders were vacuum dried. The resulting powder cakes were pulverized in a Waring blendor.

The AlN was milled with n-heptane as the milling fluid in the alumina mills for 100 hours. The milled AlN was dried in a stream of dry nitrogen without removing the alumina ($Al_2O_3$) pickup. The resulting powder cake was pulverized in a Waring blendor.

## BET and Chemical Analyses

The specific surface areas of the as-received and milled powders were determined by the BET (Brunauer, Emmett, and Teller) method. Both the as-received and milled powders were also chemically analyzed for oxygen, carbon, and trace elements. The oxygen and carbon analyses of the milled powders were used to calculate the amounts of each of the powders required to compound Sialon C. The carbon content is used in the calculations because carbon reacts with $SiO_2$ during sintering to form carbon monoxide (CO) and (presumably) silicon monoxide (SiO). Making Sialon C from the milled materials in table II required 78.99 $\alpha$-$Si_3N_4$, 16.14 AlN, and 4.87 $SiO_2$, on a weight percent basis.

## Mixing

The calculated amounts of milled $\alpha$-$Si_3N_4$, milled AlN, and milled $SiO_2$ were mixed with 5 weight percent of DC 705 silicone oil (as a temporary binder) and 70 weight percent of 200 proof ethanol. The powders were mixed for 1 hour in a polyethylene bottle with the aid of stainless steel balls. The slurry was dried at about 100° C, and the resulting powder agglomerates were pulverized in a Waring blendor.

## Cold Pressing

The powder mixture was shaped into bars approximately 3.81 by 0.92 by 0.47 centimeter by cold pressing at 207 megapascals (30 ksi) in a double-acting steel die. These bars were then isostatically cold pressed at 483 megapascals (70 ksi).

## Binder Removal

The silicone oil binder was removed from the bars by heating them slowly (in about 2 hr) in flowing nitrogen to 450° C and holding for 1 hour.

## Sintering

The bars to be sintered were placed together in a tungsten sintering boat with a close-fitting (but not gastight) cover. This boat was placed inside a larger tungsten boat fitted with a cover having a thermocouple opening. Sintering was done in a furnace with graphite heating elements for 4 hours at 1760° C in stagnant nitrogen at a 34.5-

megapascal (5-psi) gage pressure. The temperature was controlled and monitored with W/W-26Re thermocouples. The sintered bars were surface ground into 2.54- by 0.635- by 0.318-centimeter test bars. The bars to be used for MOR tests had their edges beveled 0.12 millimeter. The bars used for oxidation tests were polished to a mirror finish on a 10-micrometer diamond lap.

## Testing

The ground bars were used to determine the four-point MOR from room temperature to 1400° C in air. The silicon carbide MOR fixture used has a bottom span of 1.905 centimeters (3/4 in.) and a top span of 0.953 centimeter (3/8 in.). A silicon carbide muffle furnace mounted on an Instron tensile tester was used to heat the bars and the fixture to the test temperature. The bars were bend tested at a crosshead speed of 0.051 centimeter per minute (0.020 in./min).

Oxidation tests were carried out in air at 1400° C. During the tests the bars were held in a platinum crucible having two side holes and a loosely fitting cover, so as to allow access of air to the Sialon bars. At various times the bars were cooled, removed from the crucible and weighed in an analytical balance with microgram sensitivity. Although a few heating and cooling cycles were therefore involved in this type of oxidation test, this test is considered to be uncycled to distinguish it from the cycled oxidation test described next.

Cycled oxidation tests were carried out under the same conditions as the uncycled oxidation tests except that the bars were heated for 1-hour periods followed by 1/2 hour at room temperature. At various time intervals the cool bars were weighed in an analytical balance. In both the cycled and uncycled tests, weight gains were determined as a function of time from the weighing data. In the case of the cycled tests only the time at 1400° C was taken into account for plotting.

The densities of all the test bars were determined by water immersion. The structure of the sintered Sialon C was checked by X-ray diffraction and by optical microscopy. Scrapings from the surface of oxidized bars were used to determine the phases present by X-ray diffraction.

## RESULTS AND DISCUSSION

Reference 1 reports the results of an investigation on the effect of O/N on the sinterability of Sialons of formula $Si_{2.55}Al_{0.6}O_yN_{4-0.667y}$, where y varied from 0.157 to 0.706. Among these Sialons, the one having the composition $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$ (Sialon C in ref. 1 and this report) had the highest density (3.08 g/cm$^3$) of all the sin-

tered Sialons in the series. In addition, X-ray diffraction analysis showed it to be an essentially $\beta'$-Sialon with possible traces of X-phase. Because of its relatively high density and purity, this Sialon C was selected to determine the modulus of rupture as a function of temperature and the oxidation resistance at 1400° C.

The sintered and ground bars of Sialon C used in the present investigation had densities ranging from 3.07 to 3.10 grams per cubic centimeter, which are equivalent to 97.3 to 98.3 percent of the as-hot-pressed (or theoretical) density. An X-ray diffraction spot check showed essentially $\beta'$-Sialon with possible traces of X-phase. As shown in the photomicrograph in figure 3, Sialon C has an essentially single-phase matrix with a small amount of porosity (black), very small amounts of an Si-base alloy or compound (bright, metallic-looking), and very small amounts of a gray phase that may be either glass or polishing compound entrapped in pores.

## Modulus of Rupture

The plot of four-point MOR as a function of temperature of Sialon C is shown in figure 4. The number of bars tested and the range of MOR values are also indicated in this figure. The average strengths vary from 404 megapascals (58 600 psi) at room temperature to 254 megapascals (36 800 psi) at 1400° C. Also shown in the figure are curves for Sialons from references 3 to 6. At 1400° C only the Sialon with 2.5 weight percent $Y_2O_3$ (ref. 4) has a higher MOR than Sialon C. At lower temperatures Sialon C has lower strength than the Sialons with $Y_2O_3$ additions (refs. 3 and 4), about the same strength as the $50Si_3N_4 + 25AlN + 25Al_2O_3$ Sialon (ref. 5), and higher strength than the TLP Sialon (ref. 6).

Most of the Sialons reported in the literature show an accelerated drop in strength with increasing temperatures above about 1200° C. It is noteworthy, for this reason, that for Sialon C and for the TLP Sialon this drop in strength with temperature is much more gradual than for the other Sialons shown in figure 4. Another point worth noting regarding Sialon C is that the scatter in MOR values is about the same at all temperatures. Yet, in previous experience with other Sialons (ref. 3), the scatter decreased with increasing test temperatures. It is surmised that this decrease in scatter was probably due to the appearance of incipient plasticity (caused by the softening of the cementing phase or glass at grain boundaries). This effect plus the fact that in all tests the load-deflection curves to fracture are linear suggest that Sialon C may have better creep resistance than Sialons with $Y_2O_3$ or other additions. Also, the fact that the maximum MOR values in the scatter band are 453 and 343 megapascals (65 700 and 49 700 psi) at room temperature and 1400° C, respectively, indicates that Sialon C and similar Sialons may be amenable to a significant improvement in strength by optimizing the processing variables.

## Oxidation

The weight increases with time on oxidizing Sialon C in air at 1400° C, both with and without cycling, are plotted in figure 5. For comparison, the 1400° C oxidation behavior for hot-pressed $Si_3N_4$ (ref. 7), a Sialon with 2.5 weight percent $Y_2O_3$ (ref. 4), a Sialon with 1.11 weight percent $Y_2O_3$ (Sialon B, ref. 3), and TLP Sialon (ref. 6) is also shown in figure 5. The plots for hot-pressed $Si_3N_4$ and for TLP Sialon from references 7 and 6, respectively, were calculated from their parabolic plots because no linear plots were given. In figure 6 are shown the parabolic plots for all the materials shown in figure 5 except the Sialon from reference 4, for which the plot is so steep that it almost coincides with the ordinate.

Comparsion of the various curves in figures 5 and 6 shows that cycled and uncycled Sialon C from the present investigation have much better oxidation resistance than the other $Si_3N_4$-base ceramics shown in these figures. Like plots for other $Si_3N_4$ ceramics (refs. 7 and 8) and even pure $Si_3N_4$ (ref. 9), the plots for cycled and uncycled Sialon C in figure 6 are nonlinear at the beginning of the tests. It is surmised that this lack of linearity near the origin of the plots may be due to diffusion of impurities such as magnesium (ref. 8), surface irregularities such as grinding marks and pores, or other causes. Oxidation data showing this type of behavior can best be represented by the so-called mixed parabolic equation or general parabolic rate equation

$$\Delta W^2 = K_p t + C$$

where $\Delta W$ is the change in weight due to oxidation, $K_p$ is the parabolic rate constant, $t$ is the time, and $C$ is a constant (ref. 9). In figure 6, the plots for Sialon C become essentially linear after about 50 hours, and their slopes or parabolic rate constants are $2.8\times10^{-10}$ and $2.5\times10^{-10}$ $g^2/cm^4$ hr for cycled and uncycled Sialon C, respectively. These are smaller than the parabolic oxidation rate constants of any $Si_3N_4$-base ceramic reported in the literature.

It may be noted in figures 5 and 6 that the plots for cycled and uncycled Sialon C are smooth. In addition, the weight change of the platinum crucible in which they were oxidized was linear with time, and no debris of any kind was noted in the crucible. These facts indicate that no spalling occurred during oxidation of Sialon C. The plots also show that cycling does not significantly affect the oxidation resistance of this material. Further, comparison of the various plots in these figures shows that the oxidation resistance decreases with increasing amounts of sintering aid, as already pointed out in reference 3.

X-ray diffraction analysis of scrapings from the oxidized scale of Sialon C revealed $\alpha$-cristobalite (very strong), $\alpha$-$Si_3N_4$ (very strong), and mullite (very, very weak). This analysis is identical to that of a Sialon with 1.11 weight percent $Y_2O_3$, which is

designated Sialon B in reference 3. Therefore, X-ray diffraction analysis of the oxide scale does not provide a reliable indication of oxidation behavior.

## SUMMARY OF RESULTS AND CONCLUSIONS

The main objectives of the present investigation were to determine the modulus of rupture (MOR) as a function of temperature and the oxidation resistance at 1400° C of a Sialon without sintering aids, of composition $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$, and designated in this report as Sialon C. The results and conclusions drawn therefrom can be summarized as follows:

1. The average four-point MOR's of Sialon C range from 404 megapascals at room temperature to 254 megapascals at 1400° C. These MOR values are larger than those of any other Sialon without sintering aids reported in the literature.

2. The MOR values for Sialon C at 1400° C show very large scatter, and the drop in strength with temperature above about 1200° C is not as rapid as for Sialons with additives. In addition, in all tests the load-deflection curves to fracture were linear. These facts indicate lack of incipient plasticity at 1400° C and augur well for the creep properties of Sialon C.

3. After prolonged oxidation the parabolic oxidation rate constant for Sialon C at 1400° C is $2.5\times10^{-10}$ $g^2/cm^4$ hr as compared with $2.67\times10^{-8}$ $g^2/cm$ hr for hot-pressed $Si_3N_4$ and $19.6\times10^{-10}$ $g^2/cm^4$ hr for TLP Sialon. This parabolic rate constant for Sialon C is the smallest value for a $Si_3N_4$-base ceramic reported in the literature.

4. Cyclic oxidation tests of Sialon C at 1400° C yielded a plot of weight gain against time almost identical to that of the uncycled Sialon, and the parabolic oxidation rate constant was $2.8\times10^{-10}$ $g^2/cm^4$ hr. These results, the smoothness of the linear and parabolic plots, and the fact that no debris of any kind was found in the platinum crucible used to hold the specimens during oxidation indicate that no spalling occurred during oxidation periods of up to 200 hours.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 11, 1979,
505-01.

## REFERENCES


1. Arias, A.: Effect of Oxygen to Nitrogen Ratio on the Sinterability of Sialons. NASA TP-1382, 1979.

2. Jack, K. H.: Sialons and Related Nitrogen Ceramics. J. Mater. Sci., vol. 11, no. 6, June 1976, pp. 1135-1158.

3. Arias, A.: Pressureless Sintered Sialons with Low Amounts of Sintering Aid. NASA TP-1246, 1978.

4. Layden, G. K.: Development of Sialon Materials. (R77-912184-21, United Technologies Research Center; NASA Contract NAS3-19712.) NASA CR-135290, 1977.

5. Wills, R. R.; Stewart, R. W.; and Wimmer, J. M.: Fabrication of Reaction-Sintered Sialon. J. Am. Ceram. Soc., vol. 60, no. 1 -2, Jan. -Feb. 1977, pp. 64-67.

6. Layden, G. K.: Pressureless Sintering of Sialon Gas Turbine Components. UTRC/R77-912532-4, United Technologies Research Center, 1977. (NADC-75207-30, AD-A041207.)

7. Tripp, W. C.; and Graham, H. C.: Oxidation of $Si_3N_4$ in the Range $1300^{o}$ to $1500^{o}$ C. J. Am. Ceram. Soc., vol. 59, no. 9-10, Sept. -Oct. 1976, pp. 399-403.

8. Cubicciotti, D. D.; Jones, R. L.; and Lau, K. H.: High Temperature Oxidation and Mechanical Properties of Silicon Nitride. SRI-5522-1, SRI International, 1977.

9. Horton, R. M.: Oxidation Kinetics of Powdered Silicon Nitride. J. Am. Ceram. Soc., vol. 52, no. 3, Mar. 1969, pp. 121-124.

TABLE I. - CHARACTERIZATION OF RAW MATERIALS

| Material | Source | Manufacturer's designation | Size | Specific surface area, $m^2/g$ | Chemical analysis | | Spectrographic analysis or manufacturer's specification, ppm (unless otherwise noted) |
|---|---|---|---|---|---|---|---|
| | | | | | Oxygen, wt % | Carbon, wt % | |
| $\alpha$-$Si_3N_4$ | Kawecki Berylco Industries, Inc. | CP 85 | -325 mesh | 5.223 | 1.75 | 0.26 | Si major, 0.3 wt % Al, 0.3 wt % Ca, 200 Cr, 140 Cu, 0.3 wt % Fe, 140 Mg, 260 Mn, 300 Mo, 360 Ni, 530 Ti, 120 V, 180 Zr |
| AlN | Atlantic Equipment Engineers | AL 106 | -325 mesh | 1.83 | 2.39 | 0.11 | Al major, 70 Ca, 550 Co, 350 Cr, 90 Cu, 350 Fe, 130 Mg, 80 Mn, 250 Mo, 160 Ni, 240 Si, 190 Ti, 640 W, 140 Zr |
| $SiO_2$ | Cerac Pure | S-1061 | -325 mesh | 0.92 | (a) | 0.012 | Si major, 1000 Al, <10 Ca, 50 Cr, 120 Cu, 50 Fe, 190 Mg, 130 Mn, 90 Ti |

[a]Not determined.

TABLE II. - MILLING DATA AND CHARACTERIZATION OF MILLED POWDERS

| Milling data | | | | | Characterization of milled powders | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Powder | Mill | Media | Fluid | Time, hr | Post-milling treatment | Specific surface, $m^2/g$ | Chemical analysis | | |
| | | | | | | | Oxygen, wt % (a) | Carbon, wt % (a) | Other elements, ppm (unless otherwise noted) (b) |
| $\alpha$-$Si_3N_4$ (CP 85) | Nickel | Nickel shot | Distilled water | 300 | Leach, wash, dry | 20.33 | 6.75 | 0.47 | Si major, 0.3 wt % Al, 400 Ca, 110 Cr, 50 Cu, 0.1 wt % Fe, 60 Mg, 60 Mn, 100 Mo, 190 Ni, 170 Ti, 30 V, 30 W, 30 Zr |
| AlN (AL 106) | Alumina | Alumina | n-heptane | 100 | Dry | 9.86 | 5.04 | 0.235 | Al major, 160 Ca, 0.2 wt % Co, 0.1 wt % Cr, 80 Cu, 340 Fe, 720 Mg, 100 Mn, 380 Mo, 180 Ni, 870 Si, 50 Ti, 210 V, 690 W |
| $SiO_2$ (S-1061) | Nickel | Nickel shot | Distilled water | 130 | Leach, wash, dry | 27.1 | (c) | 0.600 | Si major, 630 Al, 130 Ca, 70 Cr, 110 Cu, 80 Fe, 210 Mg, 900 Ni |

[a]Analyses on powders treated with 5 wt % silicone oil in ethanol, mixed, then heated in flowing nitrogen for 1 hr.
[b]Values obtained by spectrographic analyses of milled and dry powders.
[c]Not determined.

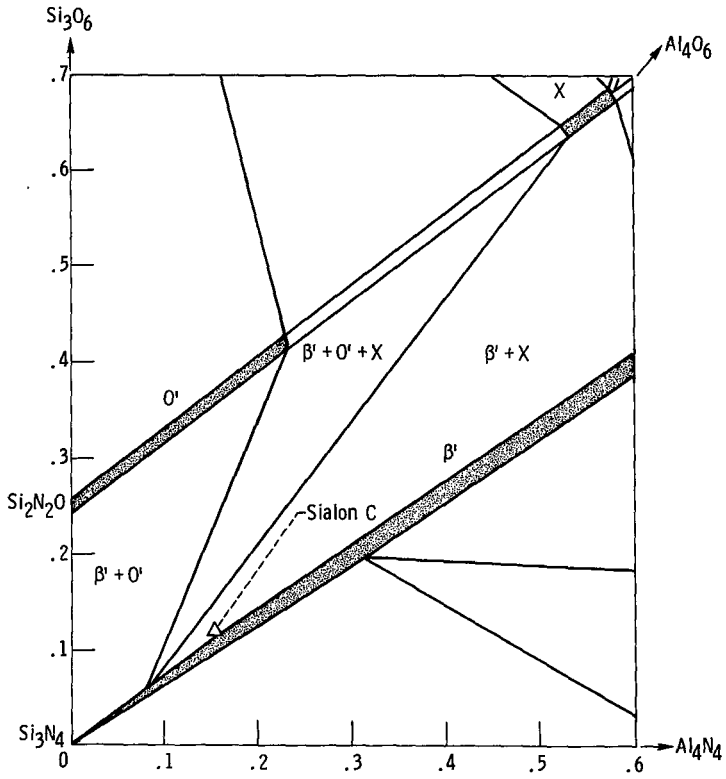


Figure 1. - $Si_3N_4$ corner of $Si_3N_4$-AlN-$Al_2O_3$-$SiO_2$ system (ref. 2) showing location of Sialon C.

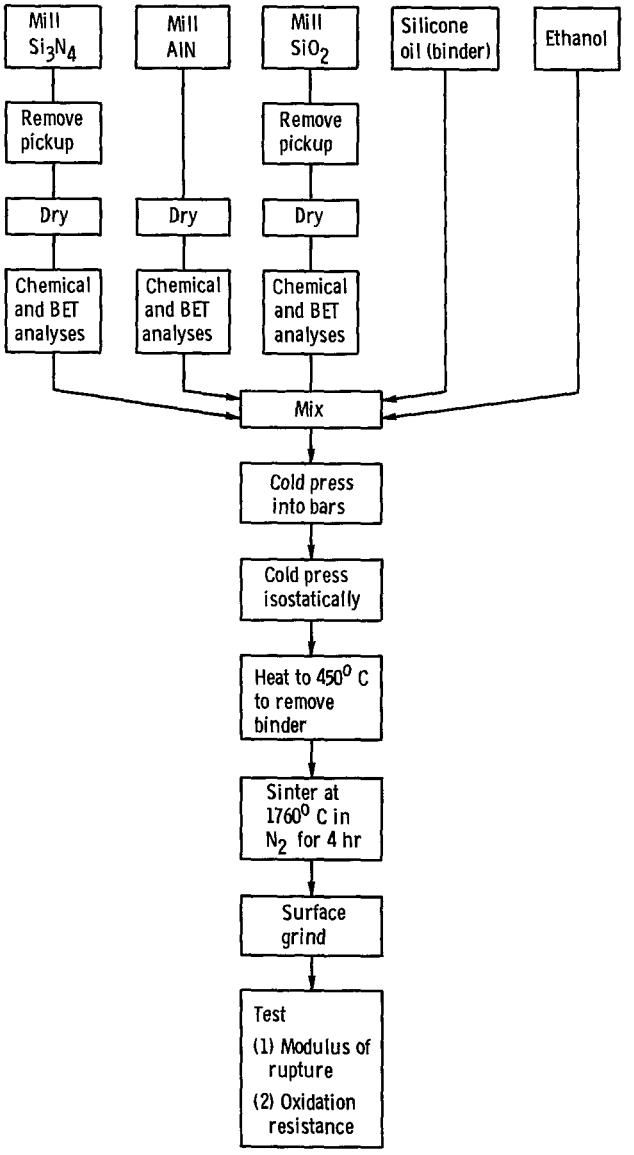


Figure 2. - Flow chart for preparation and testing of Sialon $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$

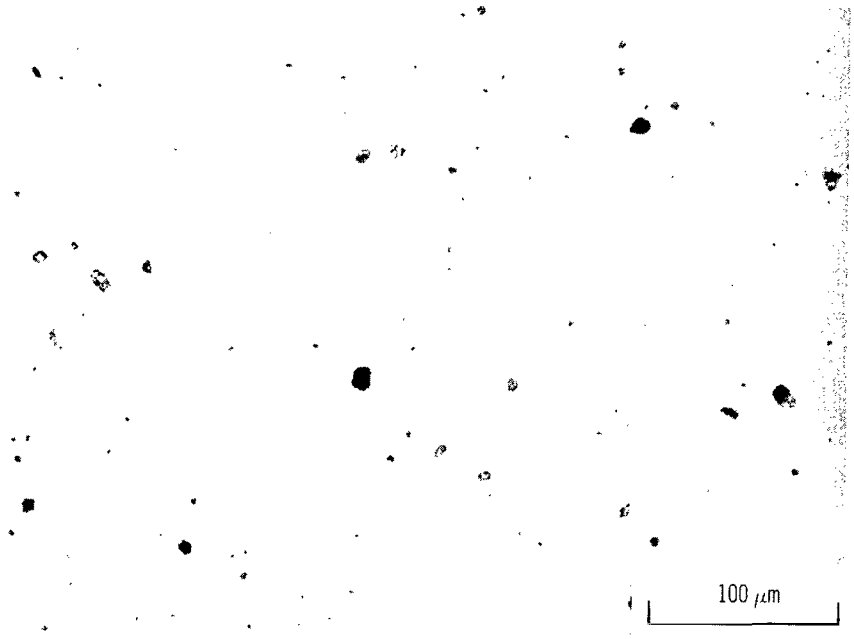


Figure 3. - Photomicrograph of Sialon C. Unetched.

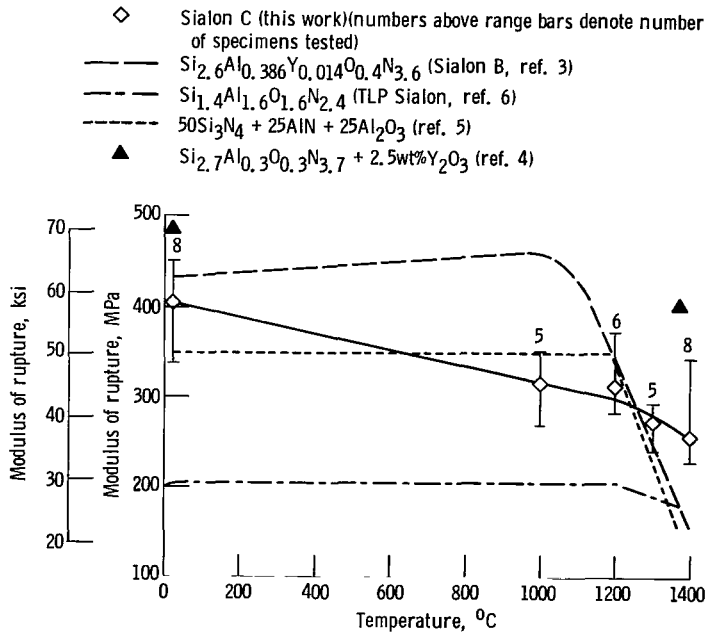


Figure 4. - Four-point modulus of rupture of various Sialons as function of temperature.

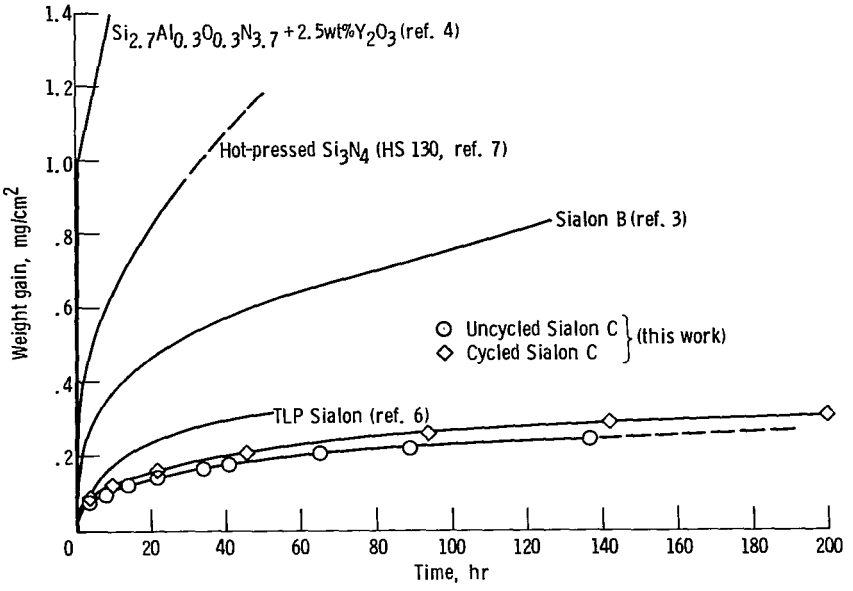


Figure 5. - Weight gain of various $Si_3N_4$-base ceramics oxidized at 1400° C in air.

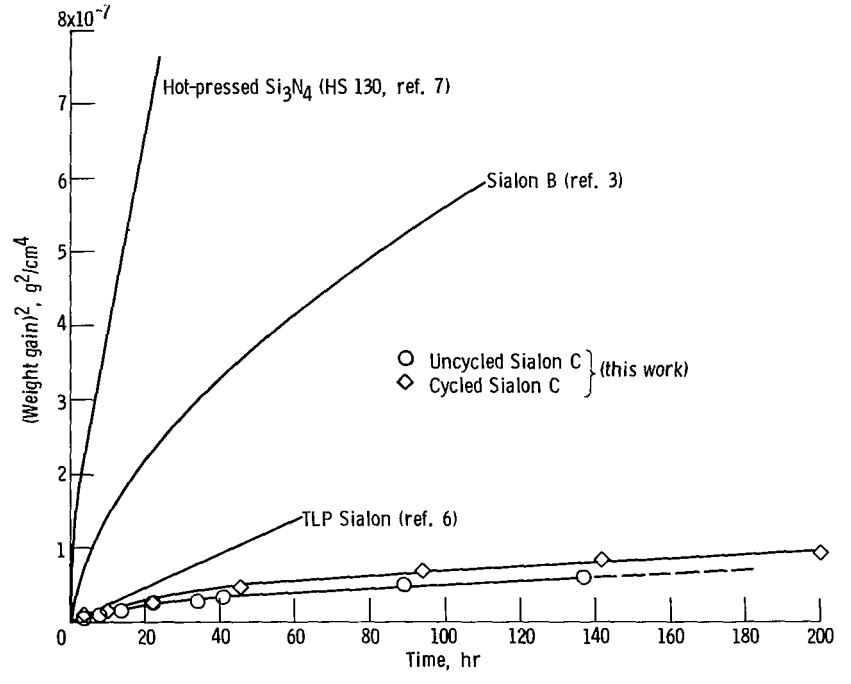


Figure 6. - Parabolic plots of oxidation of various $Si_3N_4$ ceramics at 1400° C.

| 1. Report No. | 2. Government Accession No. | 3. Recipient's Catalog No. |
|---|---|---|
| NASA TP-1490 | | |

| 4. Title and Subtitle | 5. Report Date |
|---|---|
| MODULUS OF RUPTURE AND OXIDATION RESISTANCE OF $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$ SIALON | July 1979 |
| | 6. Performing Organization Code |

| 7. Author(s) | 8. Performing Organization Report No. |
|---|---|
| Alan Arias | E-9971 |
| | 10. Work Unit No. |

| 9. Performing Organization Name and Address | 11. Contract or Grant No. |
|---|---|
| National Aeronautics and Space Administration<br>Lewis Research Center<br>Cleveland, Ohio 44135 | |
| | 13. Type of Report and Period Covered |
| 12. Sponsoring Agency Name and Address | Technical Paper |
| National Aeronautics and Space Administration<br>Washington, D. C. 20546 | 14. Sponsoring Agency Code |

15. Supplementary Notes

16. Abstract

A Sialon of formula $Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$ was made from ball-milled $\alpha$-$Si_3N_4$, AlN, and $SiO_2$ by sintering the powder compacts at 1760° C for 4 hours in stagnant nitrogen. This Sialon had an average modulus of rupture ranging from 404 megapascals (58.6 ksi) at room temperature to 254 megapascals (36.8 ksi) at 1400° C. Oxidation tests at 1400° C in air showed it to have a parabolic oxidation rate constant $\leq 2.8\times10^{-10}$ $g^2/cm^4$ hr, which is smaller than that of any other $Si_3N_4$-base ceramic reported in the literature.

17. Key Words (Suggested by Author(s))

Ceramics
Sialon
Sintering
Powder metallurgy

18. Distribution Statement

Unclassified - unlimited
STAR Category 27

| 19. Security Classif. (of this report) | 20. Security Classif. (of this page) | 21. No. of Pages | 22. Price* |
|---|---|---|---|
| Unclassified | Unclassified | 13 | A02 |

* For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1979