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# STRENGTHENING OF OXIDATION RESISTANT MATERIALS FOR GAS TURBINE APPLICATIONS

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16. Abstract

Silicon nitride and silicon carbide ceramics were treated to form compressive surface layers. The following treatments were used:

silicon carbide
- quenching
- thermal exposure

silicon nitride
- quenching
- carburizing
- carburizing and quenching

In some cases substantial improvements in impact resistance and/or flexural strength were observed. The presence of compressive surface stresses was demonstrated by slotted rod tests.

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# I. SUMMARY

In dense, fine grained ceramics fracture usually originates at surface flaws. Compressive surface stresses raise the nominal stress at which surface flaws act to cause failure. Therefore, processes that introduce these stresses can be used to strengthen ceramic materials. In earlier investigations, these processes were used to increase the tensile strength, flexural strength, thermal shock resistance, impact resistance, delayed fracture performance and resistance to penetration of surface damage of a wide variety of ceramics.

In the present investigation, the following treatments were investigated in an effort to improve the properties of silicon carbide and silicon nitride ceramics:

Silicon carbide

1. quenching
2. thermal exposure

Silicon nitride

1. quenching
2. carburizing
3. carburizing and quenching

Silicon carbide was quenched from temperatures ranging from 1900-2400°C into a variety of quenching media. The best results were obtained by quenching from 2000°C into $ZrO_2$- air fluidized beds. The presence of compressive surface stresses was demonstrated by slotted rod tests. Improvements in impact resistance and flexural strength were observed.

The beneficial effect of thermal exposure (1315°C for 50 hours in air) on the impact resistance of silicon carbide was discovered unexpectedly. Improvements in impact resistance of more than 100% were observed. The mechanism, causing this increase, is not yet understood.

Silicon nitride was quenched from temperatures ranging from 1350 to 1700°C into various liquid media. The best results were obtained by quenching from 1350 to 1400°C into silicone oil with a viscosity of 50cSt. Improvements in flexural strength of up to 30% (to 1100 $MNm^{-2}$) were observed. The impact resistance was also improved. Present evidence indicates that the principal strengthening mechanism involves a process such as flaw healing, which does not depend on quenching, together with a minor contribution due to compressive surface stresses.

Silicon nitride was carburized by packing in carburizing powders and by gas carburizing. When silicon nitride was treated by carburizing in powders, the best results were obtained by treating at 1400°C for 24 to 48 hours. Higher temperatures and longer treatment times lead to excessive evaporation. The presence of compressive surface stresses over the entire temperature range from room temperature to 1400°C was demonstrated, in several cases, by slotted rod tests. Substantial improvements in impact resistance were observed.

Silicon nitride specimens treated by gas carburization also contained compressive surface stresses.

The carburization and quenching treatments were combined. Because of testing problems, these experiments did not yield a definite result.

The results of this program demonstrate that several treatments are available which can be used to improve the strength or impact resistance of silicon carbide or silicon nitride ceramics.

## II. INTRODUCTION

### A. Background

Ceramic materials, including silicon nitride and silicon carbide, are being considered for structural applications in gas turbine engines.[1] It is expected that, if the various difficulties can be overcome, the use of these materials will permit higher operating temperatures and reduce requirements for cooling of various components.

Impact resistance, corrosion resistance, strength, and thermal shock resistance are important material properties in these applications. Various research programs having the objective of improving the impact resistance of silicon nitride and silicon carbide are underway. Among the approaches under investigation are the following:

1. Improving the strength and impact resistance by compressive surface layers.[2,3]

2. Improving the impact resistance by energy absorbing surface layers.[4,5]

3. Improving the impact resistance by fiber reinforcement.[6,7]

The objective of the present program is to improve the impact resistance of silicon nitride and silicon carbide through the use of compressive surface layers.

Compressive surface layers are widely used to strengthen brittle materials. Familiar examples include compressive glazes on whiteware and thermally and chemically "tempered" glass. Over a period of several years, Ceramic Finishing Company has developed many processes for forming compressive surface layers on a wide variety of polycrystalline ceramics and oxide single crystals.[8] These treatments improve flexural strength, tensile strength, impact resistance, thermal shock resistance, delayed fracture performance and resistance to penetration of surface damage. Polycrystalline alumina ceramics were strengthened in a number of recent investigations. These investigations were described by Kirchner, Gruver and Walker.[9-12]

Improving the impact resistance of silicon nitride and silicon carbide by compressive surface layers was investigated in a previous program. Many treatments were investigated and several yielded promising results.[2] Two of these treatments, namely, quenching of silicon carbide and carburization of silicon nitride were selected for further investigation in this program.

B. Scope and Objectives

In the present investigation, quenching of silicon carbide and silicon nitride, and carburization of silicon nitride were investigated. Three types of silicon nitride and three types of silicon carbide were treated. In Task I the treatment conditions (temperatures, time, and environment) were varied in an effort to obtain further improvements in properties. The treated specimens were evaluated by room temperature and elevated temperature impact tests and slotted rod tests and by room temperature flexural strength measurements. In Task II, the treated specimens were subjected to a 50 hour thermal exposure in air at 1315°C. The impact resistances of the specimens were measured after thermal exposure.

## III. PROCEDURES

### A. Materials

The silicon nitride and silicon carbide bodies purchased for this program are described in Table I. Materials from several different manufacturers were treated in order to provide opportunities to observe the effect of differences in the materials on the effectiveness of the treatments.

### B. Specimen fabrication

#### 1. Impact test specimens

These specimens were rectangular bars, nominally 6.4 x 6.4 x 57 mm. The bars were cut from the billets by diamond sawing. In most cases the edges of the specimens were rounded on a metal lap using diamond abrasive.

#### 2. Rod test specimens

Rod tests were used to demonstrate the presence and relative magnitude of the residual surface forces, based on the deflections when the rods were slotted. These specimens were rectangular bars, nominally 3.8 x 3.8 x 76 mm, which were cut from the billets by diamond sawing. The edges of these specimens were not rounded by lapping.

#### 3. Flexural strength test specimens

Flexural strength tests were done using specimens of various shapes and sizes. In most cases, these specimens were cylindrical rods about three or four millimeters in diameter which were left over from other projects. In other cases rectangular bars similar to the impact and rod test specimens were used.

### C. Treatments

#### 1. Quenching of silicon carbide

The principal variables in quenching treatments are the specimen shape and size, specimen temperature, the quenching medium and the quenching medium temperature. In the earlier investigation (2) impact bars were quenched from temperatures above 2000°C into various media at room temperature. Usually, thermal shock damage occurred and the impact resistances were low. On the other hand, when small cylindrical rods intended for flexural strength measurements, were quenched under the same conditions, thermal shock cracks were rarely observed and, usually, the specimens were stronger. In some cases, especially

TABLE I

MATERIALS

| Composition | Manufacturer | Grade | Forming Process | Billet Size | Density |
|---|---|---|---|---|---|
| $Si_3N_4$ | Norton | NC-132 | Hot Pressed | 6 x 6 x 1.1 in. | 3.15 Min.[1] |
| | AVCO | - | Hot Pressed | 9 x 9 x 1.1 in. | - |
| | Advanced Materials Engineering, Ltd. (AME) | - | Reaction Sintered | 6 x 6 x 0.25 in. | 2.4[2] |
| SiC | Norton | NC-203 | Hot Pressed | 9 in. diam. x 1.1 in. | 3.20 Min.[1] |
| | Alfred Ceramic Enterprises (ACE) | - | Hot Pressed | 5 in. diam. x 1.1 in. | - |
| | AVCO | - | Hot Pressed | 9 x 9 x 0.75 in. | 3.03 |

[1] Norton Company specification

[2] AME letter, dated 25 Sept. 1972

when the specimens were quenched from higher quenching temperatures (above 2200°C), the specimens were damaged by thermal shock or surface alteration and reduced strengths were observed.

Based on the above observations, a principal objective of the current program was to find quenching conditions so that impact bars could be quenched under sufficiently severe conditions to form compressive surface layers but to avoid thermal shock damage. One way to do this is to use less severe quenching media. Fluidized beds were used as the quenching media in many of these experiments.

The fluidized bed apparatus[a] used at room temperature consisted mainly of a porous plate to distribute the air flow and a large two-section can, 18 cm in diameter, to contain the fluidized bed. This apparatus, mounted beneath the induction furnace, is shown in Figure 1. The bed consisted of either zirconia[b]-air or silicon carbide[c]-air mixtures. In some cases the valve setting on the air intake was varied. Varying the valve setting varies the density of the bed and determines whether or not the specimen floats on top of the bed or the rate at which the specimen sinks slowly through the bed. With a bed using a dense granular material such as $ZrO_2$ which has a specific gravity much higher than silicon carbide, a substantial degree of control is possible.

To carry out a test, the specimen was heated in an induction furnace using a graphite susceptor. The temperature was measured by optical pyrometer. Within one minute after the desired quenching temperature was reached, the specimen was dropped into the quenching medium. Previous experience with oxide ceramics indicates that thermal shock damage can frequently be avoided by quenching from higher temperatures at which the material has higher creep rates. Therefore, specimens were quenched from various quenching temperatures in the range from 2000 to 2400°C.

Another technique used to reduce the tensile surface stresses, induced in the early stages of quenching and considered likely to cause thermal shock cracks, was to

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(a) National Polymer Products, Inc., Reading, Pa., Model 50 ALU.

(b) Titanium Alloy Manufacturing Co., Niagara Falls, N. Y., Refractory Grade $ZrO_2$, - 100 mesh.

(c) Norton Company, Worcester, Mass., Crystolon X SiC, 120 grit.

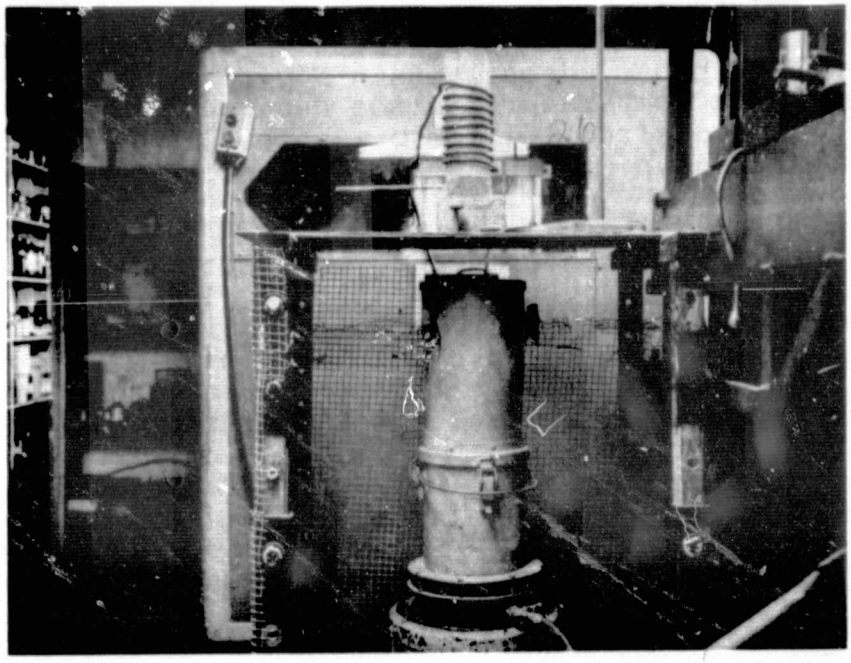

Figure 1 Fluidized bed apparatus mounted beneath the induction furnace.

quench into media held at temperatures between room temperature and the specimen temperature. Because the viscosity of the quenching medium may vary with temperature, it may not always be clear whether or not the quenching conditions are more or less severe when the quenching medium temperature is changed. The choice of elevated temperature quenching media posed some difficulties. The materials chosen were molten borax, zirconia-air fluidized beds and silicon carbide-air fluidized beds.

Considerable difficulty was encountered in building an elevated temperature fluidized bed apparatus. Several arrangements involving the use of combustion products from gas-fired furnaces were tried. In some cases, the temperatures in the fluidized beds were not as high as desired. In other cases, a thin fluidized bed could be operated at a temperature in the desired range but when a bed of the desired thickness was used, the gas-air mixture backed up causing small explosions at the air intake.

Finally, it was decided to use electrical resistance heating elements and the apparatus in Figure 2 was constructed. This apparatus makes use of a spiral silicon carbide heating element immersed in the bed which is contained in a 1 3/8 in. I.D. refractory tube. The air is introduced along the axis of the heating element and is distributed into the bed through the spaces in the spiral, in the process being heated to the desired temperature. A metal screen resting on the end of the heating element breaks up the largest air bubbles rising through the bed and prevents the specimen from falling down alongside of the heating element.

2. Thermal exposure of silicon carbide

Silicon carbide impact bars were heated for 50 hours at 1315°C in air. This post-treatment was based on an observation during Task II that the impact resistance of the silicon carbide controls improved after this thermal exposure.

3. Quenching of silicon nitride

Previous efforts to strengthen silicon nitride by quenching were unsuccessful.(8) In these earlier experiments, which were done using reaction sintered silicon nitride, it was assumed that, because of the low thermal expansion coefficient of silicon nitride, it would be necessary to use very high quenching temperatures to obtain sufficient residual compressive surface stresses.

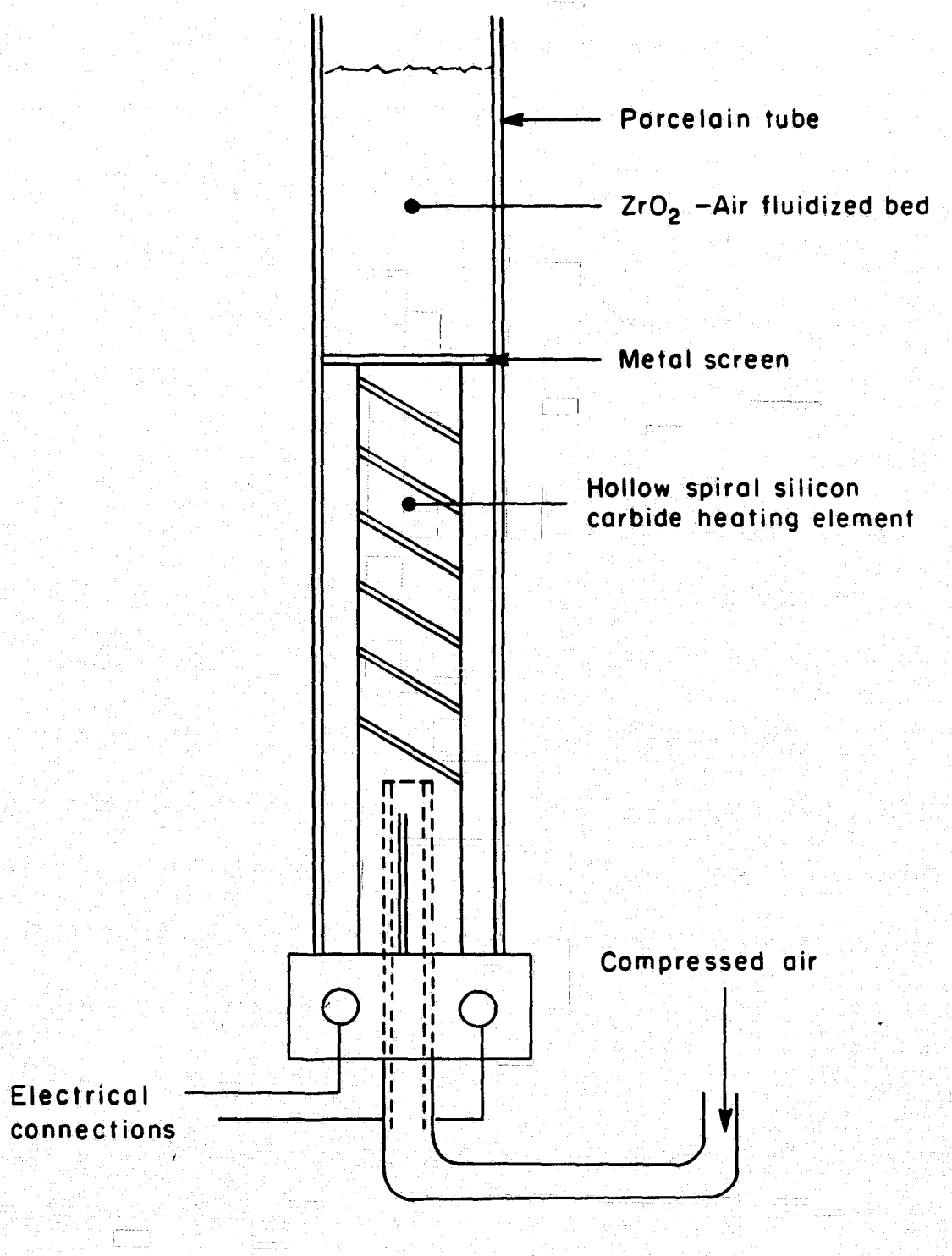


Figure 2 Elevated temperature fluidized bed apparatus.

Therefore, all of the quenching temperatures were 1500°C or higher. The highest quenching temperatures are limited by evaporation of the silicon nitride. No improvement in strength was observed in these earlier experiments.

In another recent program[4] methods were developed to form good petalite ($LiAlSi_4O_{10}$) coatings on hot pressed silicon nitride. Glazing and quenching is one of the most effective means for strengthening alumina ceramics[13]. Therefore, the initial approach to strengthening silicon nitride by quenching involved coating the specimens with petalite and quenching from moderate temperatures (1400°C) into silicone oil. These experiments were unsuccessful, apparently because the petalite coating degraded the strength of the silicon nitride. However, as part of one of these experiments an uncoated rod was quenched and an apparent increase in strength was observed. Based upon this observation, hot pressed silicon nitride rods were quenched from temperatures ranging from 1350 to 1600°C into silicone oils with viscosities ranging from 5 to 100 cSt, and into water.

4. "Carburization" of silicon nitride

The "carburization" treatments evolved from efforts in the earlier contract[2] to form silicon carbide surface layers on silicon nitride bodies. The original objective was to form silicon carbide surface layers at temperatures above room temperature but below the intended use temperature (1320°C) so that when the temperature was subsequently increased to 1320°C, the higher expansion coefficient of the silicon carbide would result in compressive surface stresses.

The silicon nitride specimens were carburized by packing in a carbon-containing powder, with or without an activator and heating at temperatures ranging from 930 to 1140°C for various periods of time. In some cases the rod tests indicated the presence of compressive surface stresses and improved impact resistances were measured. In one case the improved impact resistances were confirmed by improved flexural strengths. However, x-ray diffraction analysis failed to indicate the presence of silicon carbide in the surface so the mechanism by which the compressive stresses occurred remained unknown.

Packing experiments

Based on the experience gained in the earlier program, it was decided to continue the carburization experiments but to perform them under more controlled conditions. Previously, the specimens were packed in powders contained

in crucibles. Therefore, the silicon nitride specimens were packed in smaller diameter refractory tubes which in turn were placed in larger diameter refractory tubes. These tubes projected through an electrically heated furnace. In the majority of experiments one of two different methods of sealing the tubes was used. These methods are designated partially sealed and completely sealed. To partially seal the tube, the necked down end of the tube was cemented shut using a ceramic glaze composition. The large end of the tube was closed with a rubber stopper containing a rather long piece of glass tubing, 5.3 mm I.D., extending from it out into the room. This tubing remained open allowing equalization of pressure and slight circulation of air into the tube. To completely seal the tube, the procedure was the same as described above but a glass T was added to the long glass tube and the arms of the T were closed by two ordinary balloons which increased or decreased in size as the pressure in the furnace varied. Normally, the balloons begin to inflate when the temperature in the furnace reaches about 400°C. The maximum size is reached at about 1100°C and thereafter the size decreases slowly but the balloons remain at least partially inflated until the treatment ends. Therefore, a positive pressure of the treatment gases is maintained during the entire treatment.

Various packing materials were used including carbon black, carbon black plus activators and commercial carburizing powders. In the majority of the experiments, the packing material was NUCARB ND3000.[d] The NUCARB ND3000, used in the early experiments, was a free sample that appeared to be well mixed. When a regular quantity was received, it appeared to be inhomogeneous. Therefore, this material was mixed. Furthermore, soft white aggregates which probably were chemicals used as activators seemed to cause inhomogeneities in the surface treatment. After this was discovered, these aggregates were picked out of the packing material in the immediate vicinity of the specimens.

The treatment conditions in these experiments were varied over a wide range including temperatures up to 1450°C and treatment times up to 72 hours. The treatment time and temperature are limited by evaporation of the silicon nitride.

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[d] E. F. Houghton and Co., Philadelphia, Pennsylvania

Gas carburization

The use of gas carburization was suggested by R. L. Ashbrook of NASA Lewis Research Center. It was hoped that gas carburization would overcome some of the difficulties in the packing method including:

1. Nonuniformities caused by differences in contact of powder with the specimen surfaces.
2. Nonuniformities caused by inhomogeneities in the powder, especially in distribution of the activators.
3. Variations in pressure during the treatment cycle.

It seemed likely that improved control could be achieved using gas carburization.

Two gas carburization experiments were done. Benzene was used as the carburizing gas. Nitrogen was bubbled through the benzene and then conducted through a tube furnace which was heated to 1400°C. The first experiment involved a six hour treatment and the second one was for twelve hours. The gases escaped from the tube furnace through the necked down end of the tube. This gas stream included a substantial amount of carbon black confirming that the benzene decomposed under these conditions.

5. Carburization and quenching of silicon nitride

Combinations of treatments may yield further improvements. Therefore, carburized silicon nitride specimens were quenched, using the best quenching conditions, to evaluate these combined processes.

D. Testing

1. Impact test

The impact tests were done by the Charpy method[e] with the specimens supported on a 3.8 cm. span. In most cases, the tests were performed using a one foot pound hammer with an impact velocity of 3.4 meters per second. The room temperature specimen support consisted of a sturdy steel block with two steel rods projecting from the top. The specimen rested on the steel block and against the steel rods which were placed so that the

[e] Bell Telephone Laboratories type machine, Satec Systems, Inc., Grove City, Pennsylvania

points of contact are 3.8 cm. apart to provide the correct span. In early impact testing a specimen support fabricated from firebrick was used. This support lacked sufficient rigidity and durability so it was replaced by the steel support. A direct comparison of results obtained using cylindrical specimens of alumina gave 6% lower values using the steel test fixture than the firebrick test fixture. The data obtained using the steel support are considered to be more reliable as well as more accurate than the earlier data.

The impact testing machine was modified for elevated temperature impact testing by building an induction heated furnace and specimen support between the pendulum supports. This equipment was further modified after the previous contract(2) so that a one piece graphite channel was used as the susceptor. Alumina rods, 0.51 cm. in diameter, placed 3.8 cm. apart in holes drilled in the susceptor, were used as the load points. These alumina rods are supported from behind by the graphite channel. When properly used, the arrangement for elevated temperature impact testing yields good data.(12) However, substantial precautions are required to assure that rigidity is maintained throughout a series of tests. In some cases, this objective was not achieved, resulting in unreasonably high impact values. This problem is especially likely to arise when more impact resistant materials are tested because the more energetic impacts tend to degrade the rigidity of the system.

As a result of these difficulties, a further substantial modification of the apparatus was undertaken. By tilting the frame of the impact test machine by 15° the furnace was moved out from between the pendulum supports allowing separation of the specimen support function and the susceptor function. The new specimen support consists of a water cooled steel assembly holding two silicon nitride or silicon carbide cantilevers which in turn support the specimen. This modification of the apparatus was not completed until near the end of this contract and none of the impact test results reported herein were performed with the impact apparatus so modified.

If the modified apparatus is sufficiently rigid and durable it may be desirable to use it for both room temperature and elevated temperature measurements. If this is done, one reason for lack of comparability of the room temperature and elevated temperature data will be eliminated.

## Interpretation of impact test results

As impact resistance investigations have progressed in this laboratory during the last three years, and based upon other recently published work, our insight into the meaning of impact test results has greatly improved. Davidge and Phillips[14] pointed out that for strong, very brittle materials like ceramics, the impact "strength" (resistance) may be controlled by the elastic energy in the specimen at the instant of fracture initiation. Leuth[15] reported that, for a cemented carbide, 58% of the impact energy was energy required to elastically deflect the beam, 25% was given up to the testing machine and 9% was energy absorbed in the early stages to accelerate the specimen. The energy required to form the new surfaces was small compared with the other major contributions and this energy may be obtained from the elastic energy. Bertolotti[16] used instrumented impact testing to study factors affecting the results of impact measurements of alumina ceramics. He found that kinetic energy of the specimen and mechanical loading of the test machine introduce substantial errors in Charpy tests, especially at high impact velocities.

The energy (U) required to deflect to the fracture stress, a simply supported beam of constant cross section under the influence of a central load, can easily be derived and for rods of cylindrical cross section the resulting equation is

$$U = \frac{\pi}{24} \cdot \frac{\sigma^2 R^2 L}{E}$$

in which $\sigma$ is the maximum stress under the load,
R is the rod radius,
L is the span,
and E is Young's modulus.
Since $\pi R^2$ is the cross sectional area, this can be taken over on the other side yielding a simple equation for the deflection energy per unit cross sectional area.

In recent work, this equation was used to calculate the elastic energy necessary to deflect small cylindrical rods to the fracture stress for three point loading on a 3.8 cm. span, a situation similar to that in impact testing.[17] The fracture stresses were estimated from fracture stress-mirror size curves for impact specimens and from flexural strength tests. The elastic deflection energy ranged from 25 to 61% of the impact energy absorbed for several materials.

If the results discussed above turn out to be correct in the long run, they have important implications for the present program:

1. The impact resistance of a material consisting of a main body and surface layers that are different in some respect may depend on the effectiveness of the surface layers in deadening the blow or the effect of the surface layers on the fracture stress. In cases in which the deadening of the blow is not a factor, the impact resistance should increase with flexural strength and flexural strength should provide an adequate measure of the impact resistance.
2. If elastic deflection were the only energy absorbing mechanism, the impact resistance should increase according to the square of the flexural strength. Thus, improving the flexural strength is a relatively promising means to improve the actual impact resistance as distinguished from the measured impact resistance. Smaller increases may be observed in impact test results if the other energy absorbing mechanisms do not increase as rapidly as the elastic deflection energy. (Note that Kirchner and Gruver[12] reported that, for 96% alumina, doubling the flexural strength by quenching yielded, roughly, an 80% increase in measured impact resistance. If the elastic deflection energy was originally 30-40% of the total and this was quadrupled while all of the other factors remained the same, an increase of 80% in the measured value is reasonable.)
3. Since actual applications depend on survival of the piece and pieces may be subjected to more than one impact, the effect of sub-critical impacts on surface damage and penetration of surface damage should be investigated. Compressive surface layers may be effective in reducing penetration of surface damage and may prevent degradation of mechanical properties.[10]

2. Rod test

The rod test is used to determine the relative residual surface force induced by the treatments. For similar conditions, this test gives an indication of the relative magnitudes of the residual compressive stresses. This test has been described previously[2]. Briefly, a cylindrical rod or rectangular bar of the treated material is slotted along its axis and the deflection of the tips

of the slot is measured. If the width of the slot increases, tensile surface forces are present; if it decreases, compressive surface forces are present.

The variation in slot width was measured at temperatures ranging from room temperature to 1400°C. For the elevated temperature tests, the slotted specimen was placed along the axis of a hollow spiral silicon carbide heating element. The variation in the slot width was measured using a microscope with a calibrated eyepiece. The specimen was viewed from the end rather than from the side which was the earlier method. This method is believed to be an improvement because when the specimen was viewed from the side it was uncertain whether the front or the back of the slot was being observed.

3. Flexural strength test

Flexural strength was measured by four point loading on a 2.54 cm. span with rolling contacts. The relative humidity was controlled at about 20% during these tests. The loading rate was chosen so that one to five minutes were required to cause fracture.

E. Characterization

The methods used to characterize the materials and the effects of the treatments included x-ray diffraction analysis, electron probe microanalysis and optical and scanning electron microscopy. Since these are standard techniques they will not be described in detail. The large scale residual stresses were characterized by rod tests which were described in the previous section.

The fracture surfaces of most of the impact specimens were examined in detail by optical microscopy. The location of the fracture, whether at the center of the span or at the supports, was noted. The fracture origin was located by searching at the intersection of the fracture mirror radii and any significant features were described. If the fracture origin was at a corner of the fracture surface (edge of the original test piece), this fact was noted. Similarly, if the origin was at an edge of the fracture surface or was of internal origin, this was noted.

In some cases, the fracture mirrors were measured and the fracture stresses were estimated from fracture stress vs $(\text{mirror radius})^{-1/2}$ curves.(11,18) Using these estimates, one can determine whether or not the fracture occurred at a stress that is normal for this particular material.

# IV. RESULTS AND DISCUSSION

## A. Impact resistances of control specimens

In this section the impact resistances of control specimens of the various materials are collected and compared. This section was included because variability in the control values sometimes influenced interpretation of the results of particular experiments. Therefore, it is desirable to compare the results for a particular group of treated specimens with results for larger numbers of controls, as well as the controls for the particular experiment. Each control is identified by a specimen number. The letter, and the number following it, designate the experiment number and the last number represents the number of the specimen in the particular experiment. Using the experiment numbers, the results for treated specimens and controls from particular experiments can be compared.

### 1. Norton NC-132 silicon nitride

The impact resistances of these controls are given in Table II. At room temperature very consistent results were obtained with the overall average of about 0.36J (3.2 in. lbs.). In the first set of elevated temperature tests (G-40), unreasonably high values were observed. Previous results using other materials[4] had resulted in the expectation of values about 50% higher than those at room temperature. Another set of controls was tested (G-42) and results were obtained that were in line with the previous expectations. Examinations of the fracture surfaces of the specimens from experiment G-40 revealed very strong appearing fractures. Therefore, the high values probably are accurate. These specimens came from one of several groups that chipped badly during sawing. Therefore, the specimens were lapped much more than normally. This difference may account for the unexpected results.

### 2. Avco silicon nitride

The impact resistances of these controls are given in Table III. Although there are fewer data than desired, the results are reasonable and are consistent with the previous results obtained for AVCO silicon nitride.[4] These results are also similar to those reported in Table II for Norton NC-132 silicon nitride.

TABLE II

Impact Resistance of Norton NC-132 Silicon Nitride Control Specimens
(Nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-23-4 | Edges not rounded | 25 | 0.39 | 3.4 | broke near center, origin at corner |
| -5 | " " " | 25 | 0.33 | 2.9 | broke at center, origin at corner |
| -6 | " " " | 25 | 0.35 | 3.1 | broke at center, origin at corner |
| | | Average | 0.36 | 3.2 | |
| G-29-11 | Edges Rounded | 25 | 0.32 | 2.8 | broke at center, origin at edge, good mirror |
| -12 | " " | 25 | 0.27 | 2.4 | broke at center, origin near corner, good mirror |
| -13 | " " | 25 | 0.44 | 3.9 | broke at center, origin at edge, 6 pieces |
| | | Average | 0.34 | 3.0 | |
| G-35-9 | Edges Rounded | 25 | 0.44 | 3.9 | broke at center, origin at edge |
| -10 | " " | 25 | 0.35 | 3.1 | broke at center, origin at pore near edge |
| -11 | " " | 25 | 0.40 | 3.5 | broke at center, origin at shiny edge flaw, large mirror, 7 pieces |
| | | Average | 0.40 | 3.5 | |

Table continued on following page

See notes at end of table

TABLE II (cont.)

Impact Resistance of Norton NC-132 Silicon Nitride Control Specimens

(Nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-33-9 | Edges Rounded | 25 | 0.31 | 2.7 | broke at center, origin at edge, good mirror, 9 pieces |
| -10 | " " | 25 | 0.34 | 3.0 | broke at center, origin at corner, 8 pieces |
| -11 | " " | 25 | 0.33 | 2.9 | broke at center, origin at edge, 6 pieces |
| | | Average | 0.33 | 2.9 | |
| G-40-22 | Edges Rounded | 1320 | -[3] | - | did not break |
| -23 | " " | 1320 | 0.84 | 7.4 | broke at center, origin at corner |
| -24 | " " | 1320 | 0.67 | 5.9 | broke at center, origin at corner, no mirror(?) |
| | | Average | - | - | |
| G-42-1 | Edges Rounded | 1325 | 0.54[3] | 4.8 | broke near center, origin at corner |
| -2 | " " | 1325 | 0.61 | 5.4 | broke near center, origin at corner, no mirror (?) |
| -3 | " " | 1325 | 0.49 | 4.3 | broke near center, origin at corner |
| | | Average | 0.55 | 4.8 | |

(1) One foot pound hammer

(2) For experiments before G-33 the firebrick specimen support was used for room temperature impact tests. Subsequently the steel specimen support was used.

(3) Graphite - alumina specimen support

TABLE III

Impact Resistance of AVCO Silicon Nitride Controls

(Nominal dimensions 6.3 x 6.3 x 57.2 mm.)

| Specimen No. | Description | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-30-15 | Edges rounded | 25 | 0.41[2] | 3.6 | broke near center, origin at corner |
| -16 | " " | 25 | 0.33 | 2.9 | broke near center, internal origin |
| -17 | " " | 25 | 0.35 | 3.1 | broke near center, origin at edge, pore in mirror |
| | | Average | 0.37 | 3.2 | |
| 74-159-3 | Supplied by NASA[5] Edges not rounded | 25 | 0.34[3] | 3.0 | broke near center, internal origin |
| -4 | same as above | 25 | 0.30 | 2.6 | broke at center, internal origin, 9 pieces |
| | | Average | 0.32 | 2.8 | |
| 74-159-7 | Supplied by NASA[5] Edges not rounded | 1315 | 0.44[4] | 3.9 | broke at center, origin at edge |
| -8 | same as above | 1315 | 0.53 | 4.7 | broke at center, origin at edge |
| | | Average | 0.49 | 4.3 | |

(1) One foot pound hammer

(2) Firebrick specimen support

(3) Steel specimen support

(4) Graphite - alumina specimen support

(5) Billet #993 (H.P. $Si_3N_4$ with 0.25% by weight MgO)

3. AME reaction bonded silicon nitride

The AME reaction bonded silicon nitride was used only to a very limited extent in this program, mainly because the emphasis remained on solving the problems involved in the carburizing process rather than applying it to various materials. Therefore, measurements of controls from the particular lot of AME material purchased for this program were not done. The impact resistances of specimens supplied by NASA from another lot of material averaged 0.145J (1.25 in. lbs.).

4. ACE silicon carbide

The impact resistances of these controls are given in Table IV. The impact resistances are lower for silicon carbide than they are for silicon nitride, as expected. The elevated temperature impact resistances are higher than those at room temperature.

5. Norton NC-203 silicon carbide

The impact resistances of Norton NC-203 silicon carbide control specimens are given in Tables V and VI. The specimens from experiment F3 were cut from a small billet ordered for a previous contract(2). Compared with results on previous programs and other controls tested on the present program (F10), these values seem rather high. It is likely that at least part of this difference is caused by an actual improvement in the material because of the small size of the billet.

The data in Table VI are part of the data from a recently concluded contract(4). The specimens were cut from other large billets. The room temperature impact resistance of 0.21J (1.9 in. lbs.) seems normal. The elevated temperature values are much higher than the room temperature values as is usually observed.

6. AVCO silicon carbide

The impact resistances of these controls are given in Table VII. The values are somewhat lower than those obtained for the other types of silicon carbide tested in this investigation. Information from AVCO indicated that this material was not up to their standard density. The measured specific gravity was 3.03 which may account for the relatively low impact resistance.

0.125 in. diameter cylindrical rods were machined and polished. The average flexural strength of four specimens, measured by four point loading on a one inch

TABLE IV

Impact Resistance of ACE Silicon Carbide Control Specimens

(Nominal dimensions 6.3 x 6.3 x 57.2 mm.)

| Specimen No. | Description | Test Temp. °C | Impact Resistance (1) Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| F6-4 | Edges not rounded | 25 | 0.25(2) | 2.2 | broke at center, probable corner origin, weak fracture |
| -5 | " " " | 25 | 0.32 | 2.8 | broke at center, probable corner origin, weak fracture |
| -6 | " " " | 25 | - | - | improperly seated, fractured at support |
| | | Average | 0.29 | 2.5 | |
| F8-4 | Edges not rounded | 25 | 0.30(2) | 2.6 | broke at center, origin at corner |
| -5 | " " " | 25 | 0.15 | 1.3 | broke at center, probable corner origin, end popped off. |
| -6 | " " " | 25 | 0.27 | 2.4 | broke at center, origin uncertain |
| | | Average | 0.24 | 2.1 | |
| F8-10 | Edges not rounded | 1320 | 0.31(3) | 2.8 | broke at center, origin uncertain, weak fracture |
| -11 | " " " | 1320 | 0.37 | 3.4 | broke near center, origin at corner |
| -12 | " " " | 1320 | 0.27 | 2.5 | broke at center, unusual very weak fracture |
| | | Average | 0.32 | 2.9 | |

(1) One foot pound hammer

(2) Steel specimen support

(3) Graphite - alumina specimen support

TABLE V

Impact Resistance of Norton NC-203 Silicon Carbide Control Specimens

(Nominal dimensions 6.3 x 6.3 x 57.2 mm.)

| Specimen No. | Description | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| F3-3[2] | Edges rounded | 25 | 0.36[4] | 3.2 | 4 large pieces, origin at or near surface |
| -4 | " " | 25 | 0.33 | 2.9 | origin at or near center |
| | | Average | 0.35 | 3.1 | |
| F10-10[3] | Edges rounded | 25 | 0.22[5] | 1.9 | broke near center, origin at corner |
| -11 | " " | 25 | 0.21 | 1.9 | broke at center, origin at corner |
| -12 | " " | 25 | 0.23 | 2.0 | broke at center, origin at corner |
| | | Average | 0.22 | 1.9 | |

(1) One foot pound hammer

(2) Specimens cut from small billet originally ordered for a previous contract[2]

(3) Specimens cut from billet ordered for present contract

(4) Firebrick specimen support

(5) Steel specimen support

TABLE VI

Impact Resistance of Norton NC-203 Silicon Carbide Controls at Various Temperatures
(Nominal Dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|
| Billet No. 433646[2,3] | | | | |
| JS-52-ART | 25 | 0.21[4] | 1.9 | Break near center, origin at corner, fair mirror |
| -BRT | 25 | -- | -- | Break at center, origin at corner, poor mirror |
| -CRT | 25 | 0.21 | 1.9 | Break near center, origin at corner, fair mirror |
| | Average | 0.21[6] | 1.9 | |
| JS-52-11A | 1100 | 0.42[7] | 3.7 | Break at center, origin at corner, poor mirror |
| -11B | 1100 | 0.37 | 3.3 | Break at center, origin at corner, poor mirror |
| -11C | 1100 | 0.33 | 2.9 | Break at center and one end, origin at corner, large mirror |
| | Average | 0.37 | 3.3 | |
| JS-52-12A | 1200 | 0.49[7] | 4.3 | Break at center and one end, origin at corner, poor mirror |
| -12B | 1200 | -- | 11.0[8] | Break near center, origin at corner near inclusion, large mirror |
| -12C | 1200 | 0.47 | 4.2 | Break at center, origin at corner, poor mirror |
| | Average | 0.48[6] | 4.3 | |

Table continued on following page
See notes at end of table

TABLE VI (cont.)

Impact Resistance of Norton NC-203 Silicon Carbide Controls at Various Temperatures
(Nominal Dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|
| JS-52-13A | 1325 | 0.36[7] | 3.2 | Break at center, origin at corner, poor mirror |
| -13B | 1325 | 0.44 | 3.9 | Break near center, origin at corner, poor mirror |
| -13C | 1325 | 0.62 | 5.5 | Break at center, origin at corner, poor mirror |
| | Average | 0.47 | 4.2 | |

(1) One foot pound hammer
(2) Data from previous contract[4]
(3) Edges not rounded
(4) Steel specimen support
(5) No result, forgot to reset pointer
(6) Average of two values
(7) Graphite-alumina specimen support
(8) Specimen jammed

TABLE VII

Impact Resistance of AVCO Silicon Carbide Controls
(Nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Test Temp. °C | Impact Resistance[1] Joules | In. lbs. | Comments |
|---|---|---|---|---|---|
| B-42-1 | Edges rounded | 25 | 0.16[2] | 1.4 | broke near center, origin at corner |
| B-42-2 | " " | 25 | 0.19 | 1.7 | broke near center, origin near corner |
| B-42-3 | " " | 25 | 0.10 | 0.9 | broke at center, origin at corner, possible crack |
| | | Average | 0.15 | 1.3 | |
| | Supplied by NASA[4] | | | | |
| - | Edges not rounded | 25 | 0.11[3] | 1.0 | - |
| - | " " | 25 | 0.16 | 1.4 | - |
| - | " " | 25 | 0.16 | 1.4 | - |
| | | Average | 0.14 | 1.3 | |

(1) One foot pound hammer
(2) Steel specimen support
(3) Firebrick specimen support
(4) Billet #996 (H.P. SiC with P.P.G. powder)

span was 492 $MNm^{-2}$ (71,400 psi). This flexural strength shows that the AVCO silicon carbide is a relatively strong ceramic body in spite of the low density.

7. Specimens supplied by NASA

The impact resistances of specimens supplied by NASA are assembled in Table VIII. Some of these values were also included in previous tables. These data are representative of the impact resistances to be expected for a wide range of silicon nitride and silicon carbide materials.

B. Quenching of silicon carbide

In the earlier program, the flexural strength and impact resistance of small cylindrical rods of silicon carbide were improved by quenching.(2,3) However, when standard impact bars (6.4 x 6.4 x 57 mm.) were quenched, thermal shock cracks formed and the impact resistances were low. Therefore, one objective of this part of the present program was to find quenching conditions that would avoid thermal shock damage and then optimize those conditions to improve the flexural strength and impact resistance.

The following approaches were used to avoid thermal shock damage in the silicon carbide:

1. Less severe quenching media were used.
2. Silicon carbide specimens were quenched into media held at intermediate temperatures.
3. Specimens of silicon carbide from three different manufacturers were quenched.
4. Other heat treatments and chemical treatments were used in an effort to enhance the thermal shock resistance of the silicon carbide.

In these experiments, rod test, flexural strength test and impact test specimens were quenched into the various media using various temperatures. The properties of the quenched specimens were measured. In addition, the fracture surfaces were examined to determine whether or not the fracture features were consistent with the test results. Two fracture surfaces are compared in Figure 3. Figure 3(a) shows a weak fracture with a sharp ridge or discontinuity through the center that coincides with a thermal shock crack which is evident on the surfaces. Figure 3(b) shows a typical strong fracture surface in which the fracture originated at a corner or edge. Quenching treatments in which compressive surface stresses are demonstrated by the rod tests, improvements in impact resistance and/or flexural strength are observed and in

TABLE VIII

Impact Resistance of Specimens supplied by NASA

(Nominal dimension 6.4 x 6.4 x 50.8 mm.)

| Material | Impact Resistance | | | |
|---|---|---|---|---|
| | Room Temperature(1) | | 1320°C (2) | |
| | Joules | in. lbs. | Joules | in lbs. |
| Refel SiC #5 | 0.25 | 2.2 | 0.54 | 4.8 |
| | 0.20 | 1.8 | 0.49 | 4.3 |
| Norton SiC 3 1/8 x 3 1/8 x 35 billet | 0.29 | 2.6 | - (4) | - |
| | 0.34 | 3.1 | | |
| Norton SiC Small billet | 0.32 | 2.9 | - | - |
| | 0.33 | 2.9 | | |
| Ceradyne SiC #4 middle | 0.19 | 1.7 | 0.16 | 1.4 |
| | 0.19 | 1.7 | 0.21 | 1.8 |
| Ceradyne SiC #4A top or bottom | 0.60 | 5.3(3) | 0.18 | 1.6 |
| | 0.25 | 2.2 | 0.15 | 1.3 |
| AVCO SiC #4 from edges of 1/4" billet | 0.11 | 1.0 | no data | - |
| | 0.16 | 1.4 | 0.74 | 6.6(3) |
| AVCO SiC #2 3/8" from edge of 1/4" billet | 0.16 | 1.4 | 0.16 | 1.4 |
| AME $Si_3N_4$ #6 reaction sintered | 0.14 | 1.2 | 0.17 | 1.5 |
| | 0.15 | 1.3 | 0.66 | 5.8(3) |
| Ceradyne $Si_3N_4$ #3 middle | 0.29 | 2.6 | 0.43 | 3.8 |
| | | | 0.43 | 3.8 |
| Ceradyne $Si_3N_4$ #4 top or bottom | 0.35 | 3.1 | 0.60 | 5.3 |
| | 0.53 | 4.7 | 0.55 | 4.9 |

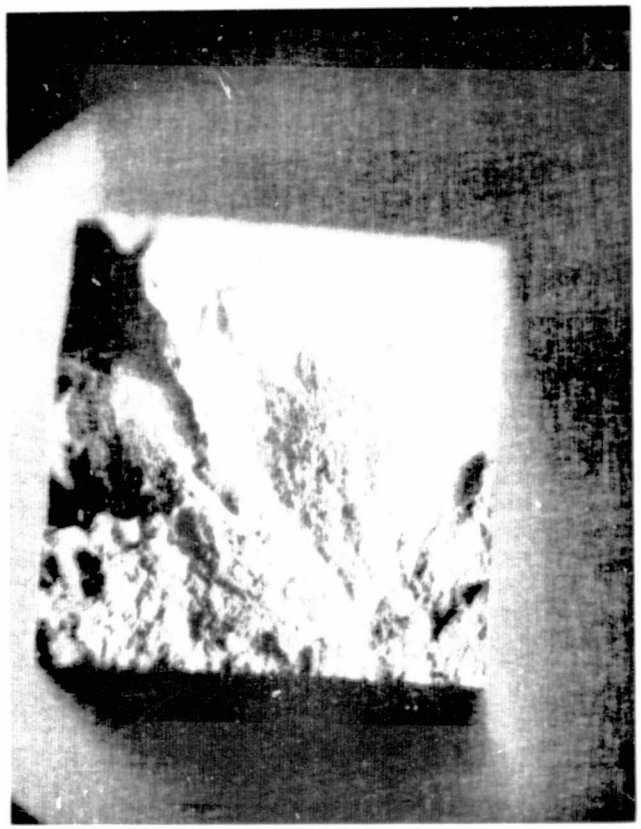
(1) Firebrick specimen support, one foot pound hammer

(2) Graphite - alumina specimen support, one foot pound hammer

(3) Specimen support may not have been rigid.

(4) Earlier data yielded unreasonably high values and has been omitted.

(a) Weak fracture in a specimen containing a thermal shock crack.



(b) Strong fracture in a specimen strengthened by quenching.

Figure 3 Comparison of fracture surfaces of quenched silicon carbide specimens with and without thermal shock cracks (10X).

which the fracture features are consistent with the other observations, are considered to have yielded reliable results.

These experiments are described in the following sections.

Less severe quenching media

The less severe quenching media chosen for investigation were fluidized beds and still air. The materials used for the fluidized beds included the combinations $ZrO_2$-air and SiC-air. Initially, ACE silicon carbide specimens were quenched into fluidized beds of these materials. Rod test results for these treatments are reported in Table IX. The negative slot deflections show that, in every case, compressive surface stresses were induced by quenching. By varying the quenching conditions, a wide range of compressive stresses was obtained. Cracks were observed in two of the specimens quenched into the SiC-air fluidized bed indicating that this is a relatively severe quenching medium.

The impact test results for ACE specimens quenched into the $ZrO_2$-air fluidized bed are presented in Tables X and XI. The impact resistances were improved at room temperature and at 1320°C. The overall average impact resistance of ACE controls at room temperature is 0.26J (2.3 in. lbs.). This compares with averages of 0.40 to 0.46J (3.5 to 4.0 in. lbs.) for the quenched specimens. At 1320°C the average impact resistance of the quenched specimens was 0.44J (3.9 in. lbs.) compared with 0.32J (2.9 in. lbs.) for the controls.

ACE silicon carbide specimens were also quenched into the SiC-air fluidized bed and the impact resistances were measured (Table XII). Because the quenching temperature was higher (2400°C) a direct comparison of the two quenching media cannot be made. However, the impact resistances of the specimens were low because of thermal stress cracks, indicating that this combination of quenching conditions was too severe for this material.

In other experiments ACE-SiC impact bars were quenched repeatedly two, three and four times, into the $ZrO_2$-air fluidized bed from 2000°C, to determine whether or not the effects of the treatment would be enhanced by repetition. Thermal shock cracks were not observed in the specimens quenched two and three times, but were observed in the specimen quenched four times. The impact resistances of these specimens were lower than control values, showing that repeated quenching, at least as done in this experiment, was not advantageous. Pitting of the surfaces

TABLE IX

Rod Test Results for ACE Silicon Carbide Specimens Quenched into Fluidized Beds or Still Air

(Nominal dimension 3.8 x 3.8 x 57.2 mm.)

| Specimen No. | Quenching Medium (Room Temperature) | Quenching Temperature °C | Slot Deflection mm |
|---|---|---|---|
| F2-A | Still air | 2000 | -0.057 |
| F2-A[1] | Still air | 2000 | -0.083 |
| F2-B | $ZrO_2$-air, full air pressure | 2000 | -0.031(1) |
| F2-B[1] | $ZrO_2$-air, full air pressure | 2000 | -0.089 |
| F4-A | $ZrO_2$-air, full air pressure | 2000 | -0.118 |
| F4-B | SiC-air, air valve 1/2 turn | 2000 | -0.119 |
| F4-C | SiC-air, air valve 1/2 turn | 2200 | -0.20(2) |
| F4-D | SiC-air, air valve 1/2 turn | 2400 | -0.30(2) |
| F9-A | $ZrO_2$-air, full air pressure | 2200 | -0.21 |
| F9-B | $ZrO_2$-air, full air pressure | 2400 | -0.27 |

(1) Specimen did not sink into quenching medium.

(2) Specimen was cracked.

TABLE X

Impact Resistance at Room Temperature of ACE Silicon Carbide Quenched into a Room Temperature $ZrO_2$-air Fluidized Bed (Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Treatment | Room Temperature[1] Impact Resistance Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| F2-1 | Edges not rounded | Quenched from 2000°C | 0.53[2] | 4.7 | origin possibly small internal pore, slightly pitted |
| F2-2 | " " " | same as above | 0.37 | 3.3 | origin at corner, thermal shock crack, pitted |
| F2-3 | " " " | same as above | 0.47 | 4.1 | origin at small pore near surface, slightly pitted |
| | | Average | 0.46 | 4.0 | |
| F6-1 | Edges not rounded | Quenched from 2000°C, full air pressure | 0.41[3] | 3.6 | broke at center and one end, origin at edge, pitted |
| F6-2 | " " " | same as above | 0.42 | 3.7 | broke near center, origin at edge, pitted |
| F6-3 | " " " | same as above | 0.53 | 4.7 | broke at center, origin not evident, pitted |
| | | Average | 0.46 | 4.0 | |
| F8-1 | Edges not rounded | Quenched from 2000°C, full air pressure | 0.44[3] | 3.9 | broke at center, origin at edge, slightly pitted |
| F8-2 | " " " | same as above | 0.35 | 3.1 | broke at center and one end, origin at edge, slightly pitted |
| F8-3 | " " " | same as above | 0.40 | 3.5 | broke at center and one end, origin at corner, pitted |
| | | Average | 0.40 | 3.5 | |

(1) One foot pound hammer

(2) Firebrick specimen support

(3) Steel specimen support

TABLE XI

Impact Resistance at 1320°C of ACE Silicon Carbide Quenched into a $ZrO_2$-Air Fluidized Bed[1]
(Nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Treatment | 1320°C[2] Impact Resistance Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| F8-7 | Edges not rounded | Quenched from 2000°C full air pressure | 0.30 | 2.6 | broke near center, origin not evident, weak fractur badly pitted |
| F8-8 | " " " | same as above | 0.47 | 4.3 | broke near center, origin at edge, few pits near fracture |
| F8-9 | " " " | same as above | 0.54 | 4.9 | broke at center, origin not evident, few pits near fracture |
| | | Average | 0.44 | 3.9 | |

(1) Room temperature fluidized bed

(2) Graphite - alumina specimen support, one foot pound hammer

TABLE XII

Impact Resistance of ACE Silicon Carbide Quenched into a SiC-air Fluidized Bed[1]
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Treatment | Room Temperature Impact Resistance[2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| F4-1 | Edges rounded | Quenched from 2400°C | 0.057 | 0.5 | thermal stress cracks |
| F4-2 | " " | " " " | 0.064 | 0.56 | thermal stress cracks |
| F4-3 | " " | " " " | 0.16 | 1.4 | thermal stress cracks |
| | | Average | 0.093 | 0.82 | |

(1) Fluidized bed at room temperature

(2) Firebrick specimen support, one foot pound hammer

was observed and may be responsible for some of the reduction in impact resistance.

Norton NC-203 silicon carbide specimens were also quenched from 2000°C into the $ZrO_2$-air fluidized bed. The room temperature impact resistances of the specimens are given in Table XIII. The first group of specimens (Experiment F3) showed an improvement in impact resistance consistent with that obtained for the ACE-SiC specimens. These specimens were cut from a small billet originally ordered for a previous contract(2). The second group of specimens (experiment F10) were weak because of thermal stress cracks. These specimens were cut from the material ordered for the present program. The third and fourth groups averaged 0.23 and 0.31 Joules (2.0 and 2.7 in. lbs.) and it is difficult to judge whether or not the impact resistances of these specimens are improved. The impact resistances of controls, cut from these larger billets and measured during the present program and a recently concluded contract, averaged from 0.18 to 0.21 Joules (1.6 to 1.9 in. lbs.) indicating the impact resistances of the above quenched specimens may have been increased.

The impact resistances measured at 1320°C of Norton NC-203 specimens quenched from 2000°C into the $ZrO_2$-air fluidized bed are given in Table XIV and averaged 0.67 Joules (5.9 in. lbs.). These results were very scattered and the fracture surfaces indicated that the fractures occurred at low stresses. Therefore, the high values may be unreliable.

In still another experiment the specimens were held at the quenching temperature for various periods of time before quenching. This experiment was based on an observation that a specimen held at the elevated temperature for a longer time seemed to be more resistant to thermal shock than specimens held only the normal time. Such an observation might be explained on the basis that more time is required to obtain a uniform high temperature in the interior of the specimen. This uniform temperature is important because, in the early stages of quenching severe tensile stresses are induced in the rapidly cooled surfaces of the piece and the only way these stresses can be reduced is by plastic flow in the interior. In the first of these experiments ACE SiC specimens broke up on heating for reasons that are not understood. In a subsequent experiment using Norton NC-203 silicon carbide specimens that were held at 2400°C for one, two and five minutes, and then quenched into a $ZrO_2$-air fluidized bed with full air pressure, thermal shock cracks were observed in all of the specimens and the impact resistances were low.

TABLE XIII

Impact Resistance of Norton NC-203 Silicon Carbide Quenched into a $ZrO_2$-Air Fluidized Bed
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Treatment | Room Temperature[1] Impact Resistance Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| F3-1[2] | Edges rounded | Quenched from 2000°C | 0.54[3] | 4.8 | broke at center, origin at corner, very strong fracture, pitted |
| -2 | " " | " " " | 0.48 | 4.2 | broke at center, origin at corner, severe pitting |
| | | Average | 0.51 | 4.5 | |
| F3-3[2] | Edges rounded | Control | 0.36[3] | 3.2 | - |
| -4 | " " | " | 0.33 | 2.9 | - |
| | | Average | 0.35 | 3.1 | |
| F10-7 | Edges rounded | Quenched from 2000°C | 0.14[4] | 1.2 | thermal shock cracks |
| -8 | " " | " " " | 0.16 | 1.4 | thermal shock cracks |
| -9 | " " | " " " | 0.09 | 0.8 | thermal shock cracks |
| | | Average | 0.13 | 1.1 | |
| F10-10 | Edges rounded | Control | 0.22[4] | 1.9 | - |
| -11 | " " | " | 0.21 | 1.9 | - |
| -12 | " " | " | 0.23 | 2.0 | - |
| | | Average | 0.22 | 1.9 | |

See notes at end of table.

Table continued on following page

TABLE XIII (cont.)

Impact Resistance of Norton NC-203 Silicon Carbide Quenched into a $ZrO_2$-Air Fluidized Bed
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Treatment | Room Temperature[1] Impact Resistance Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-37-1 | Edges rounded | Quenched from 2000°C | 0.23[4] | 2.0 | broke near center, origin at edge, large mirror, pitted |
| -2 | " " | " " " | 0.36 | 3.2 | broke near center, internal origin, few pits |
| -3 | " " | " " " | 0.34 | 3.0 | broke at center and one end, origin at edge, pitted |
| | | Average | 0.31 | 2.7 | |
| G-45-1 | Edges rounded | Quenched from 2000°C | 0.18[4] | 1.6 | broke at center, origin at corner, large mirror, weak fracture, few pits |
| -2 | " " | " " " | 0.20 | 1.8 | broke at center, origin at edge, large mirror, few pits |
| -3 | " " | " " " | 0.31 | 2.7 | broke near center, origin near surface, few pits |
| | | Average | 0.23 | 2.0 | |

(1) One foot pound hammer
(2) Specimens cut from small billet originally ordered for a previous contract[2]
(3) Firebrick specimen support
(4) Steel specimen support

TABLE XIV

Impact Resistance at 1320°C of Norton NC-203 Silicon Carbide Quenched into a $ZrO_2$-Air Fluidized Bed[1]
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Treatment | 1320°C [2] Impact Resistance Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-45-4 | Edges rounded | Quenched from 2000°C | 0.37 | 3.3 | broke at center, origin at edge, few pits |
| -5 | " " | " " " | 0.57 | 5.0 | broke near center, origin at corner, weak fracture, few pits |
| -6 | " " | " " " | 1.07 | 9.5 | broke at center, origin at edge, not a strong fracture, few pits |
| | | Average | 0.67 | 5.9 | |

(1) Fluidized bed at room temperature

(2) Graphite - alumina specimen support, one foot pound hammer

Cylindrical rods of Norton NC-203 silicon carbide were quenched from 2000°C into the $ZrO_2$-air fluidized bed and the flexural strengths were measured. These results are given in Table XV. The average flexural strength was 869 $MNm^{-2}$ (126,000 psi.). This value can be compared with an average flexural strength of 689 $MNm^{-2}$ (99,900 psi) obtained recently for a group of 50 similar control specimens tested by the same method on another current contract[f]. These results confirm that the flexural strength as well as the impact resistance is improved by the quenching treatments.

AVCO silicon carbide bars were quenched from 2000°C into the $ZrO_2$-air fluidized bed at room temperature. The results are given in Table XVI. At room temperature the highest value is reasonable for a control or slightly strengthened specimen and the other two values are very low. Examination of the fracture surfaces indicated that all three specimens fractured at low stresses and even the specimen with the highest impact resistance may have been damaged by thermal stresses. The fracture surfaces of the specimens tested at 1320°C indicated that these specimens also failed at relatively low stresses in spite of the rather high impact resistances. Therefore, the principal conclusion of these experiments is that the quenching conditions were too severe for this material.

Quenching into media at elevated temperatures

One way to reduce the thermal stresses during quenching is to raise the temperature of the quenching medium. If other factors that affect the rate of heat transfer, such as the viscosity of the medium, remain approximately unchanged, raising the temperature of the medium should result in less severe quenching conditions and reduced thermal shock damage.

Various quenching media were considered. The media selected for investigation were borax, the $ZrO_2$-air fluidized bed, and the SiC-air fluidized bed.

Borax was chosen as a quenching medium because it has a desirable variation of viscosity with temperature (viscosity is low enough at the desired quenching temperatures to insert the specimens without undue force but it is still quite viscous), it is readily available, and

[f] Contract N00019-73-C-0356

TABLE XV

Flexural Strength of Norton NC-203 Silicon Carbide
Quenched from 2000°C into a Zirconia-Air
Fluidized Bed (1)
(Rod diameter 3 mm.)

| Specimen No. | Flexural Strength (2) $MNm^{-2}$ |
|---|---|
| G-47-1 | 936 |
| G-47-2 | 844 |
| G-47-3 | 827 |
| Average | 869 |

(1) Fluidized bed at room temperature
(2) Four point loading on a one inch span

TABLE XVI

Impact Resistance of AVCO Silicon Carbide Quenched into $ZrO_2$-air Fluidized Bed
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Description | Treatment | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|---|
| G-46-1 | Edges rounded | Quenched from 2000°C | 25 | 0.24[2] | 2.1 | broke at center, origin uncertain, weak fracture, very few pits |
| -3 | " " | " " " | 25 | 0.069 | 0.6 | broke at center, origin uncertain, weak fracture, very few pits |
| -5 | " " | " " " | 25 | 0.077 | 0.7 | broke near center, origin at corner, weak fracture, very few pits |
| | | | Average | 0.13 | 1.1 | |
| B-42-1 | Edges rounded(?) | Control | 25 | 0.16[2] | 1.4 | - |
| -2 | " " | " | 25 | 0.19 | 1.7 | - |
| -3 | " " | " | 25 | 0.10 | 0.9 | - |
| | | | Average | 0.15 | 1.3 | |
| G-46-2 | Edges rounded | Quenched from 2000°C | 1320 | 0.44[3] | 3.9 | broke at center, origin uncertain, weak fracture, few pits |
| -4 | " " | " " " | 1320 | 0.50 | 4.4 | broke at center, origin uncertain, weak fracture, very few pits |
| -6 | " " | " " " | 1320 | 0.25 | 2.2 | broke at center, origin uncertain, weak fracture, very few pits |
| | | | Average | 0.40 | 3.5 | |

(1) One foot pound hammer (2) Steel specimen support
(3) Graphite-alumina specimen support

it is not too corrosive to refractory containers. ACE SiC impact specimens and rod test specimens were quenched from various temperatures ranging from 2000 to 2300°C into the borax at temperatures ranging from 800 to 1000°C. The rod tests indicated that compressive surface forces similar in magnitude to those obtained by other quenching treatments were achieved. However, the impact specimens were damaged by thermal stresses and the impact resistances were low. Some of the specimens were pretreated by heating in air at 1400°C and by heating in borax at 800, 900, or 1000°C. The objective of these pretreatments was to increase the resistance of the specimens to thermal shock. There was no conclusive evidence that these pretreatments were effective. Examination of the specimens showed cracks parallel to the long sides of the specimens. In some cases ridges were observed in the fracture surfaces that coincided with these cracks. These results indicate that the quenching conditions were too severe for this material.

Norton NC-203 silicon carbide specimens were quenched from various temperatures into $ZrO_2$-air and SiC-air fluidized beds held at 650 or 800°C. The results of these experiments are given in Table XVII. In some cases individual specimens survived the quenching without cracking and improved impact resistance was observed. In other cases, the specimens were cracked and the impact resistances were low. Efforts to obtain higher temperatures in the fluidized beds were unsuccessful. Since the best results obtained by quenching into elevated temperature fluidized beds were not as good as the best results for room temperature fluidized beds, this work was discontinued.

Thermal exposure of quenched specimens

Norton NC-203 silicon carbide impact bars were quenched from 2000°C into the $ZrO_2$-air fluidized bed at room temperature and then exposed to a furnace treatment in air for 50 hours at 1315°C. The quenched and thermally exposed specimens were impact tested at room temperature. The impact resistances are given in Table XVIII and show that the specimens were degraded by the thermal exposure. Essentially, the improvement expected as a result of quenching was lost as a result of subsequent thermal exposure.

Examination of these specimens revealed that the surfaces were badly pitted. Many of the pits were associated with particles of zirconia that adhered to the surface during the quenching step. Apparently, these particles subsequently reacted with the silicon carbide during the period of thermal exposure, causing the degradation in impact resistance. The degradation did not occur because of relief of the residual stresses by creep. This

TABLE XVII

Impact Resistance of Norton NC-203 Silicon Carbide Specimens
Quenched into Fluidized Beds at Elevated Temperatures
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Quenching Medium | Quenching Furnace Temp. °C | Quenching Medium Temp. °C | Room Temp. Impact Resistance (1) Joules | in. lbs. | Comments |
|---|---|---|---|---|---|---|
| G-43-1 | $ZrO_2$-Air | 2200 | 650 | -- | -- | cracked |
| G-43-2 | " " | 2200 | 650 | -- | -- | cracked |
| G-43-3 | " " | 2000 | 650 | 0.36 | 3.2 | broke near center, origin at corner, few pits |
| G-43-4 | " " | 2000 | 650 | 0.31 | 2.7 | broke near center, origin at edge, few pits |
| G-43-5 | " " | 2200 | 800 | 0.20 | 1.8 | broke near center, origin at edge, few pits |
| G-43-6 | " " | 2200 | 800 | 0.10 | 0.9 | cracked, surface alteration |
| G-43-7 | " " | 2400 | 800 | -- | -- | cracked |
| G-43-8 | Air (2) | 2000 | 25 | 0.42 | 3.7 | broke near center, origin uncertain, severe pitting |
| G-43-9 | SiC-air | 2200 | 650 | 0.07 | 0.6 | cracked |
| G-43-10 | " " | 2200 | 650 | 0.25 | 2.2 | broke at center, origin at corner, a few severe pits |
| G-43-11 | " " | 2400 | 800 | 0.16 | 1.4 | broke near center, origin at frothy flaw, a few severe pits |

(1) Steel specimen support, one foot pound hammer

(2) Specimen missed fluidized bed and fell on floor.

TABLE XVIII

Impact Resistance of Norton NC-203 Silicon Carbide, Quenched into a Room Temperature $ZrO_2$-air Fluidized Bed and Thermally Exposed[1]

(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Test Temp. °C | Impact Resistance[2] Joules | in lbs. | Comments |
|---|---|---|---|---|
| G-52-7 | 25 | 0.24[3] | 2.2 | corner origin |
| -8 | 25 | 0.12 | 1.1 | large frothy inclusion |
| -9 | 25 | 0.33 | 2.9 | corner origin |
| | Average | 0.23 | 2.1 | |
| B-51-1 | 25 | 0.17[3] | 1.5 | internal origin |
| -2 | 25 | 0.26 | 2.3 | edge origin |
| -3 | 25 | 0.07 | 0.7 | many large pores under surface |
| | Average | 0.17 | 1.5 | |
| B-53-1 | 1315 | 0.21[4] | 1.9 | weak fracture |
| -2 | 1315 | 0.61[5] | 5.7 | weak fracture |
| -3 | 1315 | 0.22 | 2.0 | weak fracture |
| | Average | 0.22[6] | 2.0 | |

(1) Quenched from 2000°C, thermally exposed at 1315°C for 50 hours in air

(2) One foot pound hammer

(3) Steel specimen support

(4) Graphite - alumina specimen support

(5) This high value should be disregarded because the fracture surface indicated fracture occurred at low stresses.

(6) Average of two values

mechanism can only be significant at much higher temperatures. Presumably, the degradation caused by pitting and reaction with the adhering zirconia can be prevented by using other quenching media.

C. Thermal Exposure of silicon carbide

One of the treatments specified for Task II of this program involved exposure of treated specimens and controls at 1315°C in air for 50 hours. The impact resistances of the thermally exposed controls were found, unexpectedly, to be substantially higher than those of controls that were not thermally exposed. Lange[19] exposed hot pressed silicon carbide containing cracks formed by thermal shock to air at 1400°C for various periods of time and measured the flexural strengths. Healing of the cracks by oxidation occurred but the increase in strength with time at 1400°C was very small, only about 5 to 10% compared to the unheated thermally shocked material. Therefore, the mechanism of the increase in impact resistance observed in the present experiments is not yet understood. The results of the present thermal exposure experiments are presented in the following paragraphs .

Norton NC-203 silicon carbide impact specimens were thermally exposed as described above and the impact resistances were measured at room temperature and 1315°C with the results given in Table XIX. Because the impact resistances were higher than expected, these results were originally considered to be incorrect so that the experiment was partly repeated by another technician. These results for impact tests at room temperature are also included in Table XIX and, essentially, they confirm the results of the first experiment. Therefore, this increased impact resistance of the thermally exposed Norton NC-203 silicon carbide must be considered to be a real effect.

ACE silicon carbide impact specimens were also thermally exposed. The impact resistances of these specimens, measured at room temperature and at 1315°C are given in Table XX. Comparison of these results with the controls indicates no significant difference in impact resistance as a result of the thermal exposure. It is reasonable that differences in composition or microstructure could result in differences in response of the two types of silicon carbide to thermal exposure.

TABLE XIX

Impact Resistance of Thermally Exposed[1]
Norton NC-203 Silicon Carbide

(Nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Test Temp. °C | Impact Resistance[2] Joules | in. lbs. | Comments |
|---|---|---|---|---|
| B-51-1C | 25 | 0.55[3] | 4.9 | edge origin |
| B-51-2C | 25 | 0.44 | 3.9 | - |
| B-51-3C | 25 | 0.48 | 4.3 | - |
| | Average | 0.49 | 4.4 | |
| B-53-1C | 1315 | -[4] | - | did not fracture |
| B-53-2C | 1315 | 1.06 | 9.4 | corner origin |
| B-53-3C | 1315 | 0.77 | 6.8 | corner origin |
| | Average | 0.92 | 8.1 | |
| G-52-10 | 25 | 0.50[3] | 4.4 | small internal mirror |
| G-52-11 | 25 | 0.67 | 5.9 | corner origin |
| G-52-12 | 25 | 0.47 | 4.2 | small internal mirror |
| | Average | 0.55 | 4.8 | |

(1) Heated in an electric furnace at 1315°C for 50 hours in air
(2) One foot pound hammer
(3) Steel specimen support
(4) Graphite - alumina specimen support

TABLE XX

Impact Resistance of Thermally Exposed[1]
ACE Silicon Carbide

(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Test Temp. °C | Impact Resistance[2] Joules | in. lbs. | Comments |
|---|---|---|---|---|
| 74-163-7 | 25 | 0.27[3] | 2.4 | broke near center and one end, internal origin at shiny spot. |
| -8 | 25 | 0.29 | 2.5 | broke at center, internal origin |
| -9 | 25 | 0.29 | 2.5 | broke near center, origin at edge |
| | Average | 0.28 | 2.5 | |
| 74-163-10 | 1315 | 0.35[4] | 3.1 | broke near center and one end, origin uncertain |
| -11 | 1315 | 0.23 | 2.0 | broke near center, origin uncertain |
| -12 | 1315 | 0.21 | 1.8 | broke at center, origin at large flaws near corner |
| | Average | 0.26 | 2.3 | |

(1) Heated in an electric furnace at 1315°C for 50 hours in air

(2) One foot pound hammer

(3) Steel specimen support

(4) Graphite - alumina specimen support

D. Quenching of silicon nitride

Earlier efforts[8] to improve the flexural strength of silicon nitride failed, apparently because the specimens were degraded by heating to the high temperatures that were used (1500-1825°C). A high quenching temperature was believed to be necessary to induce sufficient thermal stresses during rapid cooling. Otherwise, because the thermal expansion coefficient of silicon nitride is low, inadequate thermal stresses were expected. Because of this previous experience, petalite ($LiAlSi_4O_{10}$) coatings were used in the present investigation in an attempt to avoid the degradation of the silicon nitride. Previously, these coatings were used as energy absorbing surface layers[4].

Cylindrical rods of Norton NC-132 silicon nitride were coated with petalite(g) and fired at 1400°C for 45 minutes under reducing conditions. The coated specimens were quenched from various temperatures in the range from 1400 to 1700°C into silicone oil (100 cSt.). The flexural strengths were measured and are presented in Figure 4. In some cases the fracture stresses were determined from fracture stress vs. $(\text{fracture mirror radius})^{-1/2}$ curves as described by Kirchner and Gruver[18], and are plotted in place of the flexural strengths. The strengths of the quenched specimens were low but the strengths of the coated but unquenched specimens were also low, indicating that the coating process degraded the strength and that subsequent quenching had little or no effect on the strength of the degraded specimens.

In one of the above experiments an uncoated rod was quenched from 1400°C and was found to have substantially increased strength. Based on this result it was decided to investigate lower quenching temperatures. The results are given in Figure 5 and show that the flexural strength was improved for specimens quenched from 1350 to 1400°C. Then, similar specimens were quenched from 1350 or 1400°C into media of varying viscosity. Little variation of strength with viscosity was observed but the best results were obtained by quenching from 1350°C into silicone oil with a viscosity of 50 cSt. (Figure 6). The strength of these specimens averaged 1100 $MNm^{-2}$ (160,000 psi.), about 30% higher than the control values. Specimens quenched into water were damaged by thermal shock so that, during flexural testing, both specimens broke outside the region of uniform maximum stress with fractures originating at thermal shock damage.

(g) Ceramic Color and Chemical Mfg. Co., New Brighton, Pa.

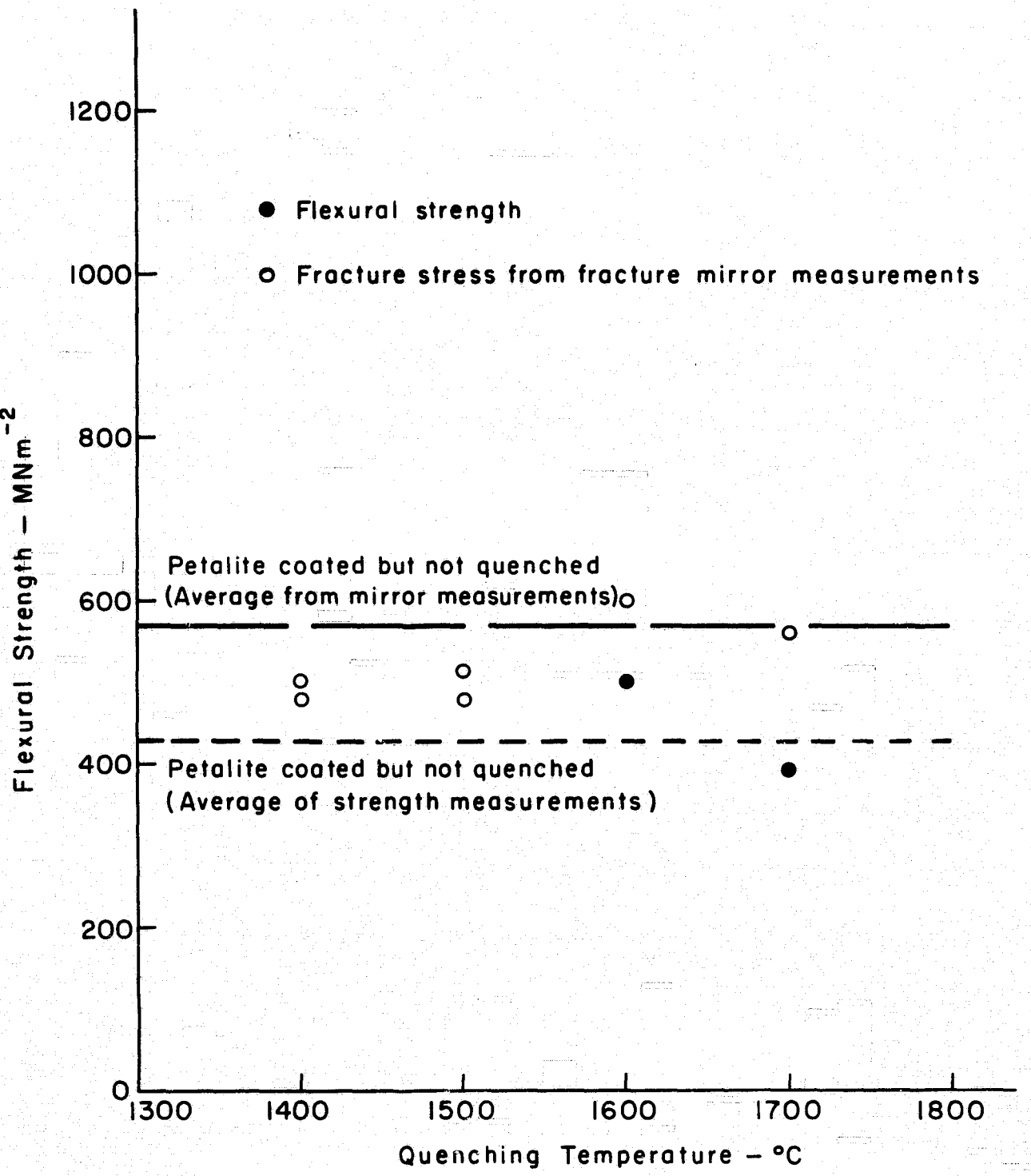



Figure 4 Flexural strength vs. quenching temperature for Norton NC-132 silicon nitride rod specimens with petalite coatings, quenched into silicone oil (100 cSt.). (Four point loading on a one inch span).

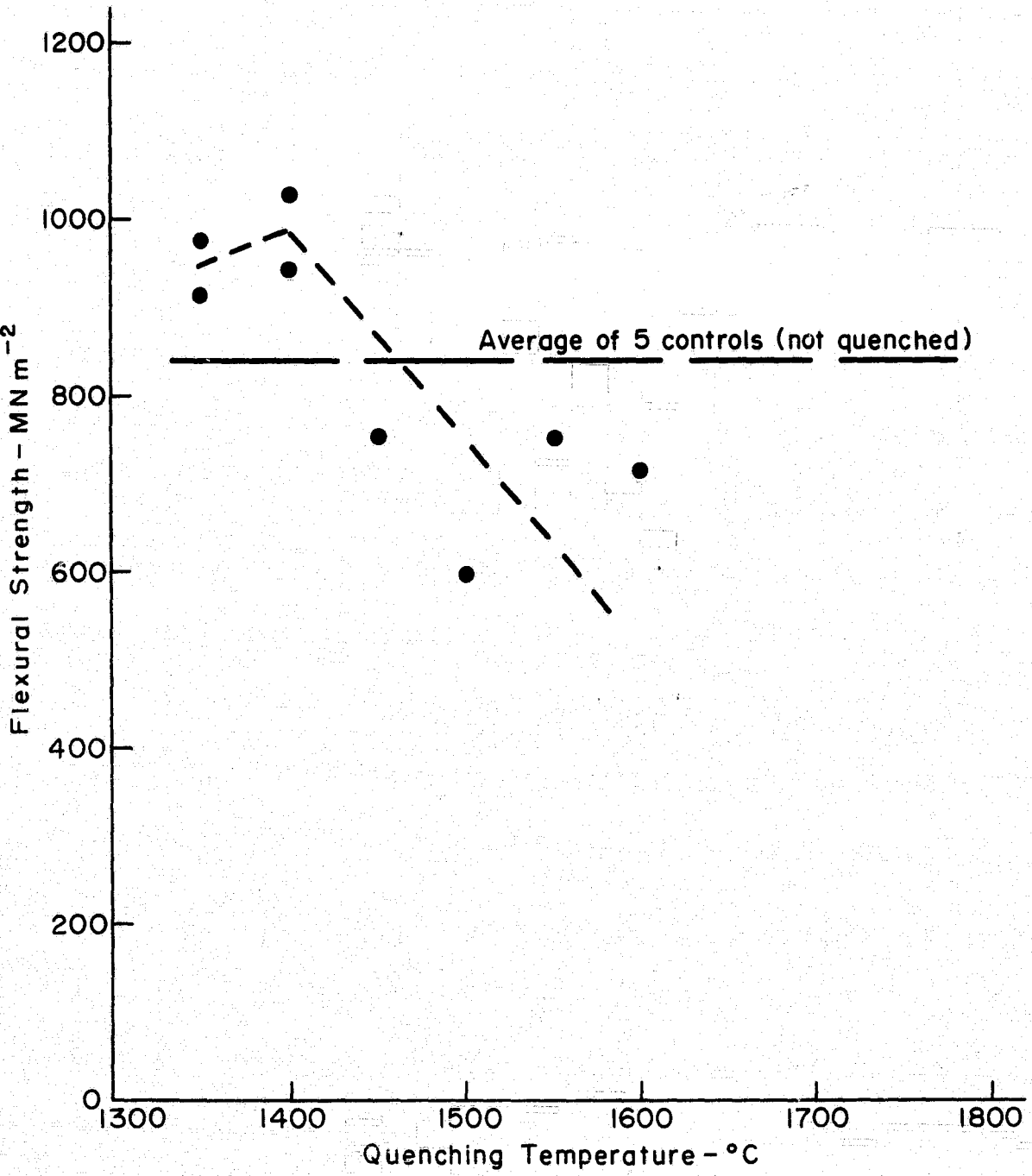



Figure 5 Flexural strength vs. quenching temperature for Norton NC-132 silicon nitride rod specimens quenched into 100 cSt. silicone oil. (Four point loading on a one inch span).

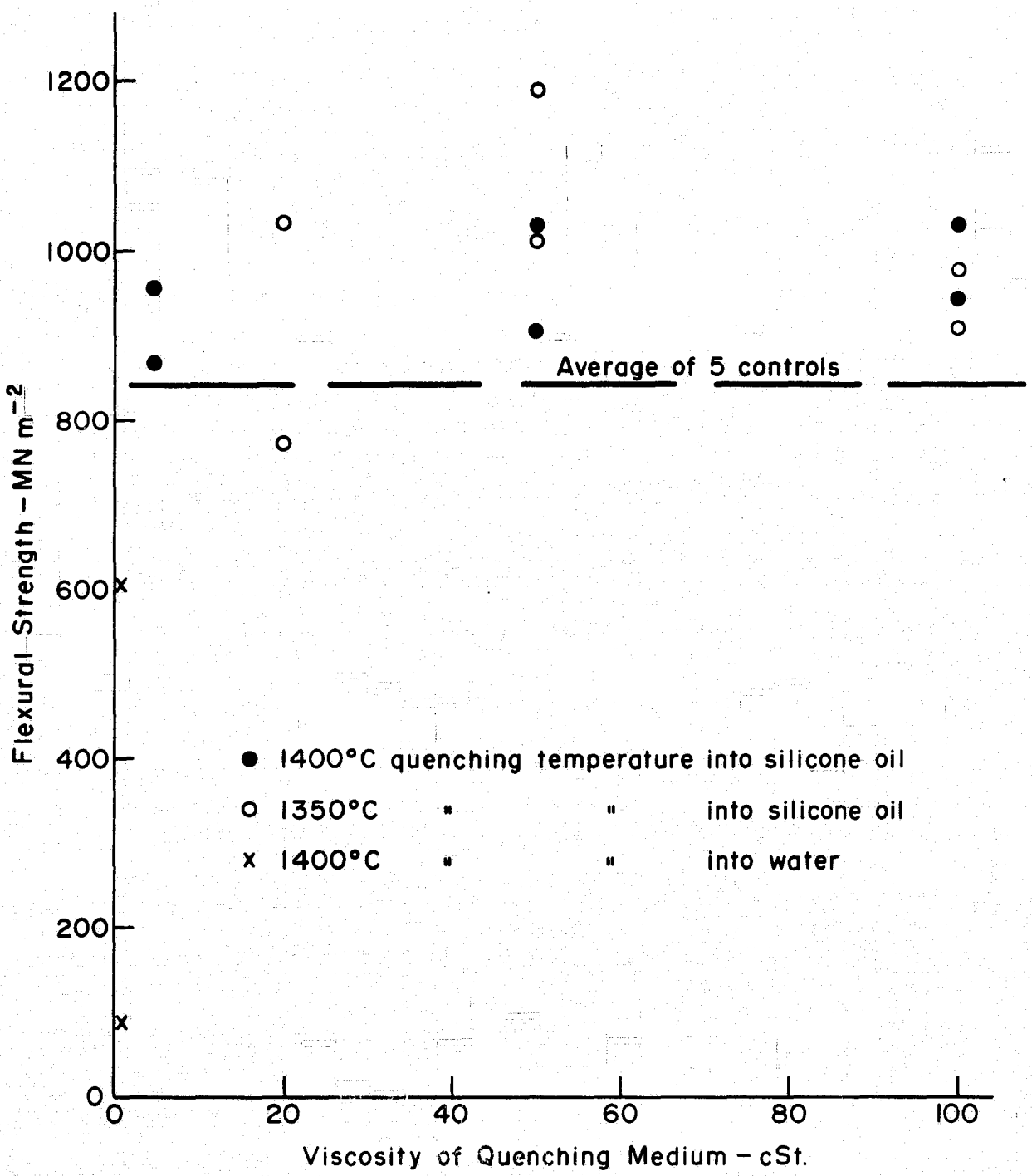



Figure 6 Flexural strength vs. viscosity of quenching medium for Norton NC-132 silicon nitride rod specimens quenched into silicone oils and water. ( Four point loading on a one inch span).

Impact specimens were also quenched from 1350°C into 50 cSt. silicone oil. As shown in Table XXI, the impact resistances of these specimens averaged 0.62J which was higher than the control value. This control value seems higher than normal so that the improvement may be greater than indicated by these results.

In interpreting the above improvements in flexural strength and impact resistance, it is important to consider the possibility that the observed improvements may occur as a result of flaw healing, reduction of stress corrosion as a result of the presence of residual silicone oil, or other mechanisms than compressive surface stresses. Since this experimental work ended, these mechanisms have been investigated under another contract[h]. Protection by silicone oil did not increase the strength. Residual stress estimates based on fracture mirror measurements indicated that moderate residual compressive surface stresses were present, but rod tests yielded inconclusive results. However, refiring followed by slow cooling yielded a substantial increase in strength. Therefore, present evidence suggests that the major strengthening effect should be attributed to a mechanism that does not depend on quenching, such as a flaw healing, with a minor (<50%) contribution due to compressive surface stresses.

E. Carburizing of silicon nitride

1. Packing in carburizing powders

Comparison of oxidizing and carburizing treatments

Variations in packing material, gaseous environment, and treatment time and temperature were used in efforts to optimize the treatments. In the first experiment, Norton NC-132 hot pressed silicon nitride rod test specimens were exposed to various oxidizing and carburizing conditions at temperatures ranging from 1130 to 1400°C and for periods of 24 or 48 hours. The specimens were evaluated by means of the slotted rod test and by x-ray diffraction analysis of the surfaces. The results are given in Table XXII.

Specimens 1, 2, 6 and 9 were exposed to oxidizing conditions. Apparently, at 1130°C, the treatment temperature was too low to cause significant changes, other than the slight weight gain caused by formation of a thin, uniform oxidation layer. At 1400°C, the temperature is so high that both severe oxidation and evaporation occur so that substantial weight loss and bubble formation in the oxidation layer are observed. On the other hand, at 1300°C, there is a substantial weight gain as a result of oxidation but the temperature is not high enough to

(h) Contract N00014-74-C-0241

TABLE XXI

Impact Resistance of Norton NC-132 Silicon Nitride
Quenched from 1350°C into 50 cSt. silicone oil

(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Room Temp. Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|
| 1 | Quenched | 0.58 | 5.2 | broke near center, origin at corner, 12 pieces |
| 2 | Quenched | 0.59 | 5.2 | broke near center, internal origin, 12 pieces |
| 3 | Quenched | 0.69 | 6.1 | broke near center, origin at edge, 10 pieces |
| | Average | 0.62 | 5.5 | |
| 4 | Control | 0.38 | 3.3 | broke near center, unusual break, origin at edge, 7 pieces |
| 5 | Control | 0.64 | 5.7 | broke several pieces, origin near corner, 13 pieces |
| 6 | Control | 0.62 | 5.5 | broke at center, origin at edge, 18 pieces |
| | Average | 0.55 | 4.8 | |

(1) Steel specimen support, one foot pound hammer

TABLE XXII

Oxidizing and Carburizing Treatments
(Norton silicon nitride rod test specimens, nominally 3.8 x 3.8 x 76 mm.)

| Specimen No. | Treatment Description | Room Temp. Rod Test(1) | Elevated Temp. Rod Test | Tentative Phase Identification | Comments |
|---|---|---|---|---|---|
| G-19-1 | 1130°C for 24 hours in air (slight weight gain) | no change | no change to 1400°C | $\beta$-$Si_3N_4$, $\alpha$-$SiO_2$(2), enstatite | little surface alteration |
| G-19-2 | 1130°C for 24 hours in flowing $O_2$ (slight weight gain) | no change | no change to 1400°C | $\beta$-$Si_3N_4$, $\alpha$-$SiO_2$ | little surface alteration |
| G-19-3 | 1130°C for 24 hours packed in carbon black, sealed tube (slight weight gain) | no change | no change to 1400°C | $\beta$-$Si_3N_4$, $Si_2ON_2$ | little surface alteration, dark patches |
| G-19-4 | 1130°C for 24 hours packed in carbon black, flowing $O_2$ (slight weight gain)' | no change | no change to 1400°C | slight peak broadening and shifting to lower angles | little surface alteration |
| G-19-6 | 1400°C for 24 hours in air (substantial weight loss) | no change | opened .051 mm. on heating to 1400°C returned to zero on cooling | $\alpha$-$SiO_2$, no $\beta$-$Si_3N_4$ | severe oxidation and bubble formation |
| G-19-7 | 1130°C for 24 hours packed in NUCARB ND3000, open to air (slight weight gain) | -.03 mm. | closed additional .03 mm on heating; returned to -.03 mm. on cooling | possible $\alpha$-$SiO_2$, $\beta$-$Si_3N_4$ | dark bumps on 3 surfaces |
| G-19-8 | 1130°C for 24 hours packed in NUCARB AC, open to air (slight weight gain) | +.061 mm. | tensile surface forces at all temperatures | $\beta$-$Si_3N_4$ peaks shifted to lower angles and broadened, possible $\alpha$-$SiO_2$ | dark bumps, spaced |
| G-19-9 | 1300°C for 24 hours in air (substantial weight gain) | -.061 mm. | lower compressive surface forces at elevated temperatures | $\beta$-$Si_3N_4$, $\alpha$-$SiO_2$, enstatite | smooth, light grey surface |
| G-19-10 | 1200°C for 24 hours in NUCARB ND3000, open to air (substantial weight loss) | +.061 mm. | tensile surface forces at all temperatures | peak broadening due to SS., possible $\alpha$-$SiO_2$ | dull black surface |
| G-19-11 | 1200°C for 48 hours in NUCARB ND3000, open to air | packing burned up | | | |
| G-19-12 | 1200°C for 48 hours in NUCARB ND3000, partially sealed (substantial weight gain) | -.091 mm. | lower compressive surface forces at elevated temperatures | not determined | dark bumps |

(1) + indicates slot opened (tensile stresses), - indicates slot closed (compressive stresses)

(2) $\alpha$- $SiO_2$ refers to $\alpha$or low cristobalite

cause substantial evaporation. These observations of the effect of oxidizing conditions may be useful for interpretation of differences observed for specimens carburized under conditions described as partially or completely sealed.

Specimens 3, 4, 7 and 8 were carburized at 1130°C by packing in various powders. Specimen 7 which was packed in NUCARB ND3000 and was open to air showed the presence of compressive stresses in the surface at room temperature. During the rod test, these stresses increased with increasing temperature to 1400°C. The presence of the compressive stresses over the entire temperature range was unexpected but is considered to be very desirable because of the possibility of improved impact resistance at all temperatures. Based on the original objective of forming silicon carbide surface layers, tensile stresses would have been expected at room temperature and compressive stresses above the carburizing temperature. This behavior was observed in the earlier program[2] but silicon carbide was not identified in the surfaces.

Specimens 10, 11, and 12 were packed in NUCARB ND3000 and treated at 1200°C for 24 or 48 hours. Compressive surface stresses were observed in specimen 12 which was treated for 48 hours at 1200°C partially sealed. In this case, the compressive stresses decreased slightly with increasing temperature to 1400°C but compressive stresses were present over the entire temperature range.

The experiments described above show that compressive surface stresses can result from both oxidation treatments and carburization treatments with some oxygen present.

The conditions used for additional carburizing treatments are summarized in Table XXIII. The objectives of these experiments were to evaluate several combinations of time and temperature, to compare the effects of oxidation and carburization, and to determine whether repacking several times would enhance the effect of carburization. Based upon the rod test results, it appears that treatments at 1400°C for 24 hours are the most effective. The presence of the carburizing medium is essential to obtain compressive stresses at 1200°C. The compressive stresses were not observed for specimens treated in air at 1200°C, but as shown in Table XXIII compressive stresses are induced by treatment at 1300°C. The weight loss was very substantial (several percent) in some of the experiments and this may be a limiting factor at high temperatures and long treatment times. Repacking was not effective under the conditions chosen for the experiment.

TABLE XXIII

Additional Oxidizing and Carburizing Treatments

(Norton silicon nitride rod test specimens, nominally 3.8 x 3.8 x 76 mm.)

| Specimen No. | Treatment Description | Room Temp. Rod Test mm | Elevated Temp. Rod Test |
|---|---|---|---|
| G-24-1 | 1200°C for 24 hours in NUCARB ND-3000, completely sealed (slight weight gain) | +0.025 | Opened to 790°C then closed again |
| G-24-2 | 1300°C for 24 hours in NUCARB ND-3000, partially sealed (substantial weight loss) | No change | Opened to 1200°C then closed again |
| G-24-3 | 1200°C for 24 hours in carbon black +3% $BaCO_3$, completely sealed (slight weight gain) | +0.025 | No change |
| G-25-1 | 1400°C for 24 hours in NUCARB ND-3000 partially sealed (substantial weight loss) | -0.051 | Closed to 1400°C. |
| G-25-2 | Same, completely sealed (substantial weight loss) | -0.076 | Closed to 1400°C |
| G-25-3 | 1200°C for 24 hours in air, partially sealed (very slight weight gain) | No change | No change |
| G-25-4 | Same, completely sealed (very slight weight loss) | No change | No change |
| G-25-5 | 1200°C for 72 hours packed in NUCARB ND-3000, partially sealed (weight loss) | -0.038 | Closed to 1400°C |
| G-25-6 | Same, completely sealed (weight loss) | -0.025 | Closed to 1400°C |

TABLE XXIII (cont.)

Additional Oxidizing and Carburizing Treatments

(Norton silicon nitride rod test specimens, nominally 3.8 x 3.8 x 76 mm.)

| Specimen No. | Treatment Description | Room Temp. Rod Test mm | Elevated Temp. Rod Test |
|---|---|---|---|
| G-28-1 | 1200°C for 24 hours in NUCARB ND-3000(1), completely sealed (substantial weight loss) | No change | Little change |
| G-28-2 | 1200°C for 48 hours in NUCARB ND-3000, completely sealed, repacked after 24 hours (slight weight loss) | No change | Opened slightly to 1400°C |
| G-28-3 | 1200°C for 72 hours in NUCARB ND-3000 completely sealed, repacked after 24, 48 hours (substantial weight loss) | No change | - |
| G-28-4 | 1200°C for 96 hours in NUCARB ND-3000, completely sealed, repacked after 24, 48, 72 hours (substantial weight loss) | No change | - |
| G-28-5 | 1200°C for 24 hours in NUCARB ND-3000, partially sealed (substantial weight loss) | No change | - |
| G-28-6 | 1200°C for 48 hours in NUCARB ND-3000, partially sealed, repacked after 24 hours (substantial weight loss) | No change | - |

(1) New lot of NUCARB ND-3000

TABLE XXIII (cont.)

Additional Oxidizing and Carburizing Treatments

(Norton silicon nitride rod test specimens, nominally 3.8 x 3.8 x 76 mm.)

| Specimen No. | Treatment Description | Room Temp. Rod Test mm | Elevated Temp. Rod Test |
|---|---|---|---|
| G-28-7 | 1200°C for 72 hours in NUCARB ND-3000, partially sealed, repacked after 24, 48 hours (very substantial weight loss) | no change | - |
| G-28-8 | 1200°C for 96 hours in NUCARB ND-3000, partially sealed, repacked after 24, 48, 72 hours (very substantial weight loss) | +0.051 | - |
| G-29-5 | 1400°C for 24 hours in NUCARB ND-3000, completely sealed (very substantial weight loss) | -0.051 | No change |
| G-29-10 | 1400°C for 24 hours in NUCARB ND-3000, partially sealed (very substantial weight loss) | -0.025 | Opened to 1400°C Tensile stresses at 1400°C |

The results of two elevated temperature rod tests are presented in Figures 7 and 8. These particular results show that the compressive surface stresses are retained throughout the entire temperature range and are even greater at high temperature than at room temperature. This result is considered to be of major importance because the presence of compressive surface stresses over the entire temperature range should result in improved impact resistance over the entire temperature range.

Impact resistance of carburized Norton silicon nitride

In searching for the best treatment conditions, Norton NC-132 silicon nitride impact specimens were carburized at temperatures ranging from 1200 to 1450°C and for periods of time ranging from eight to 72 hours. Some of the experiments were repeated several times. To reduce confusion in presentation of the data, the results are presented in order of increasing treatment temperature and, at each temperature, in order of increasing time in Table XXIV.

Treatments at 1200°C did not yield consistent improvements. The first group (experiment G-23) averaged 0.47 Joules (4.1 in. lbs.), an improvement compared with most of the control values but the next three groups (experiments G-30 and G-33) failed to confirm this result. Other specimens, treated for 72 hours, may have been improved but two high values observed for specimens that fractured at the supports rather than at the center of the span, probably should be considered an accidental result of the testing method.

The treatment at 1350°C for eight hours apparently was successful and resulted in an improvement in impact resistance at room temperature of about 50%.

Treatments at 1400°C yielded improvements in impact resistance in most cases. The average room temperature impact resistances ranged from 0.33J (2.9 in. lbs.) to 0.68J (6.0 in. lbs.). The average elevated temperature impact resistances ranged from 0.55J (4.8 in. lbs.) to 0.80J (7.1 in. lbs.). The best elevated temperature results were obtained for specimens treated for 36-40 hours, partially sealed (experiment G-40). Since the elevated temperature impact resistance is of more practical importance than room temperature impact resistance, this may be the most promising of these results. Also, at 1400°C treatments for long periods of time, such as 72 hours, result in substantial evaporation, so that these longer treatments seem less practical.

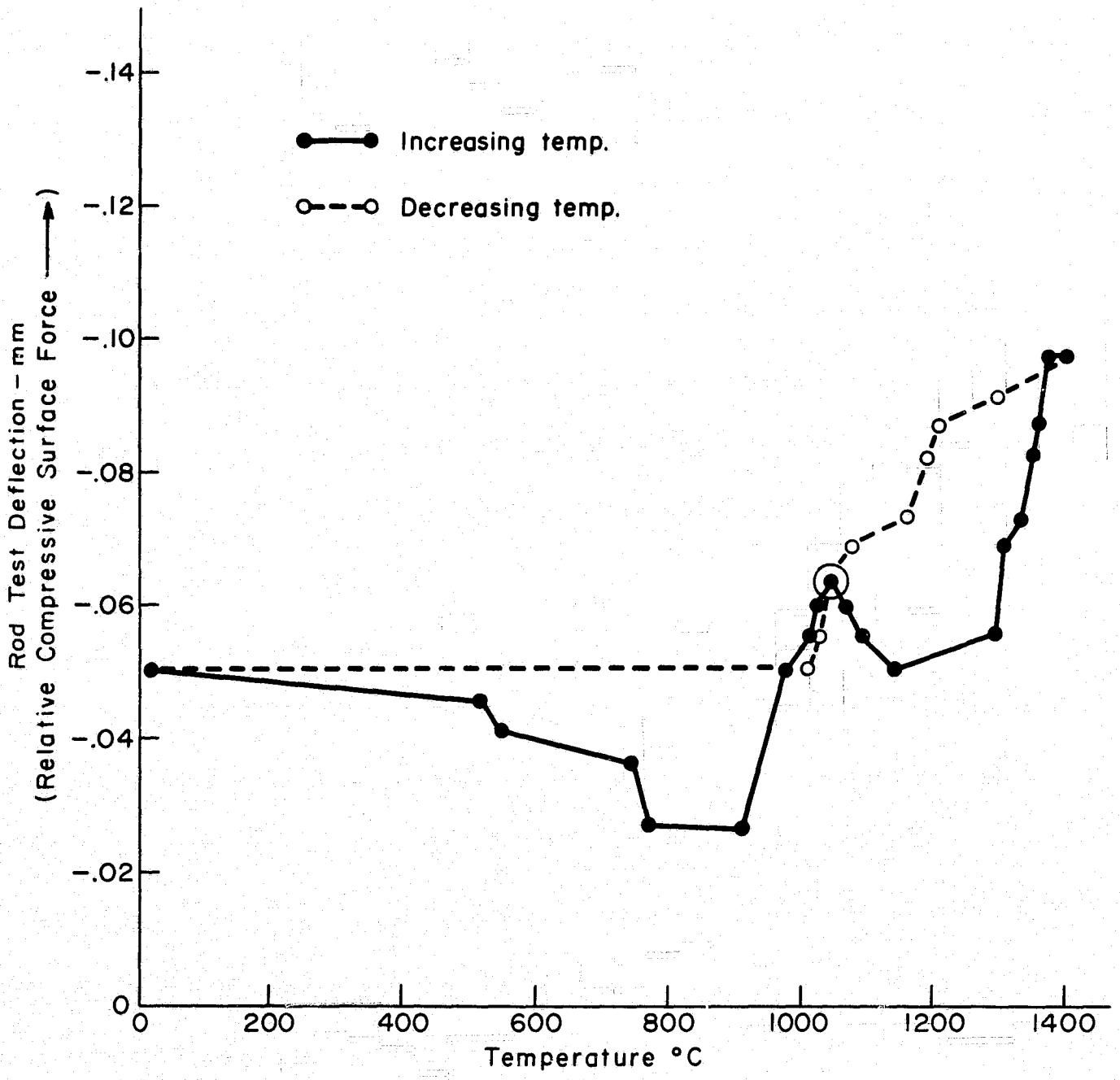



Figure 7 Elevated temperature rod test, Norton NC-132 silicon nitride packed in NUCARB ND 3000, 1400°C, 24 hours, partially sealed (G-25-1).

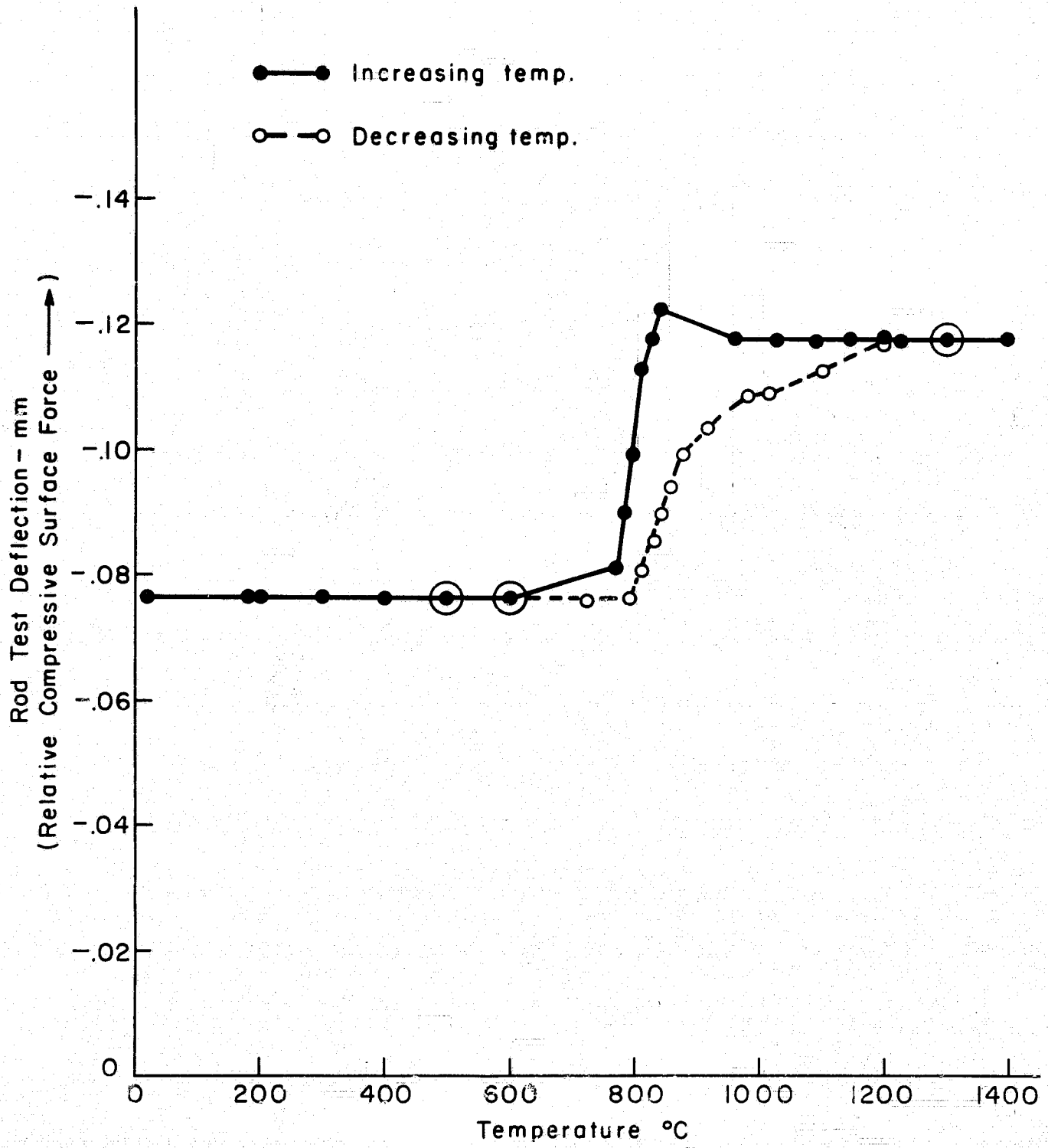



Figure 8 Elevated temperature rod test, Norton NC-132 silicon nitride packed in NUCARB ND 3000, 1400°C, 24 hours, completely sealed (G-25-2).

TABLE XXIV

Impact Resistance of Carburized Norton Silicon Nitride
(Packed in NUCARB ND 3000, nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-23-1 | 1200°C, 48 hours, partially sealed | 25 | 0.58[3] | 5.2 | strong looking fracture surface, origin at corner |
| G-23-2 | " " " " | 25 | 0.39 | 3.4 | good mirror, wedge with arc |
| G-23-3 | " " " " | 25 | 0.43 | 3.8 | good mirror, origin at corner |
| | | Average | 0.47 | 4.1 | |
| G-30-2 | 1200°C, 48 hours, partially sealed | 25 | 0.31 | 2.7 | broke at center, origin at corner, loose surface layer |
| G-30-3 | " " " " | 25 | 0.29 | 2.6 | broke at center, origin at edge, loose surface layer |
| G-30-4 | " " " " | 25 | 0.36 | 3.2 | - |
| | | Average | 0.32 | 2.8 | |
| G-33-1 | 1200°C, 48 hours, partially sealed | 25 | 0.33 | 2.9 | broke at center, origin at corner |
| G-33-2 | " " " " | 25 | 0.43 | 3.8 | broke at center, origin at or near corner |
| G-33-3 | " " " " | 25 | 0.32 | 2.8 | broke at center, origin at edge |
| | | Average | 0.36 | 3.2 | |

See notes at end of table.

Table continued on following page.

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride
(Packed in NUCARB ND 3000, nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-33-5 | 1200°C, 48 hours, completely sealed | 25 | 0.31 | 2.7 | - |
| G-33-6 | " " " " | 25 | 0.34 | 3.0 | - |
| G-33-7 | " " " " | 25 | 0.31 | 2.7 | - |
| | | Average | 0.32 | 2.8 | |
| G-25-1 | 1200°C, 72 hours, completely sealed | 25 | 1.19 | 10.5 | fracture originated at support |
| G-25-2 | " " " " | 25 | 1.33 | 11.9 | fracture originated at support |
| G-25-3 | " " " " | 25 | 0.46[4] | 4.1 | origin at corner |
| | | Average | - | - | |
| G-25-4 | 1200°C, 72 hours, partially sealed | 25 | 0.50[4] | 4.4 | origin at corner |
| G-25-5 | " " " " | 25 | 0.38[4] | 3.4 | origin at internal flaw, shiny spot, good mirror |
| G-25-6 | " " " " | 25 | 0.40[4] | 3.5 | origin at corner |
| | | Average | 0.43 | 3.8 | |

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride

(packed in NUCARB ND 3000, nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs | Comments |
|---|---|---|---|---|---|
| G-30-8 | 1350°C, 8 hours, partially sealed | 25 | 0.55 | 4.9 | broke near center, origin at corner |
| G-30-9 | " " " " | 25 | 0.38 | 3.4 | broke at center, origin at corner |
| G-30-10 | " " " " | 25 | 0.61 | 5.4 | broke at center, origin at edge |
| | | Average | 0.51 | 4.6 | |
| G-26-1 | 1400°C, 24 hours, completely sealed | 25 | 0.54[4] | 4.8 | origin at corner |
| G-26-2 | " " " " | 25 | 0.66[4] | 5.8 | probable origin at corner |
| G-26-3 | " " " " | 25 | 0.49[4] | 4.3 | probable origin at corner |
| | | Average | 0.56 | 5.0 | |
| G-29-1 | 1400°C, 24 hours, completely sealed | 25 | 0.28 | 2.5 | broke at center, origin at edge, reddish gray color |
| G-29-2 | " " " " | 25 | 0.47 | 4.2 | broke near center, origin at edge, loose reddish gray surface layer |
| | | Average | 0.38 | 3.4 | |

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride

(Packed in NUCARB ND 3000, nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-29-6 | 1400°C, 24 hours, partially sealed | 25 | 0.53 | 4.7 | broke at center, origin at edge, loose reddish gray surface layer |
| G-29-7 | " " " " | 25 | 0.47 | 4.2 | broke at center and one end, origin at shiny internal flaw |
| | | Average | 0.51 | 4.5 | |
| G-29-3 | 1400°C, 24 hours, completely sealed | 1320 | 0.72[5] | 6.4 | broke at center, origin at edge, loose green surface layer |
| G-29-4 | " " " " | 1320 | 0.60 | 5.3 | broke near center, origin at flaw near edge, loose green surface layer |
| | | Average | 0.67 | 5.9 | |
| G-29-8 | 1400°C, 24 hours, partially sealed | 1320 | 0.61[5] | 5.4 | broke near center, origin at edge, loose green surface laye |
| G-29-9 | " " " " | 1320 | 0.58 | 5.1 | broke at center, origin at edge, loose green surface lay |
| | | Average | 0.60 | 5.3 | |

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride

(Packed in NUCARB ND 3000, nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp °C | Impact Resistance[1,2] Joules | in. lbs | Comments |
|---|---|---|---|---|---|
| G-35-1 | 1400°C, 24 hours, completely sealed | 25 | 0.36 | 3.2 | broke at center and end, origin at edge |
| G-35-2 | " " " " | 25 | 0.36 | 3.2 | broke at center, origin at edge |
| G-35-3 | " " " " | 25 | 0.49 | 4.3 | broke at center, origin at edge, small mirror |
| | | Average | 0.41 | 3.6 | |
| G-35-5 | 1400°C, 24 hours, partially sealed | 25 | 0.62 | 5.5 | broke near center, origin at corner, small mirror |
| G-35-6 | " " " " | 25 | 0.49 | 4.3 | broke at center, origin at edge |
| G-35-7 | " " " " | 25 | 0.46 | 4.1 | broke at center, origin at or near edge |
| | | Average | 0.52 | 4.6 | |
| G-44-2 | 1400°C, 24 hours, completely sealed | 25 | 0.32 | 2.8 | broke near center, origin at edge |
| G-44-3 | " " " " | 25 | 0.40 | 3.6 | broke at center, origin at edge |
| G-44-4 | " " " " | 25 | 0.36 | 3.2 | broke at center, origin at edge |
| | | Average | 0.36 | 3.2 | |

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride
(Packed in NUCARB ND 3000, nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-44-9 | 1400°C, 24 hours, partially sealed | 25 | 0.41 | 3.7 | broke at center, origin at corner |
| G-44-10 | " " " " | 25 | 0.43 | 3.8 | broke at center, origin uncertain |
| G-44-11 | " " " " | 25 | 0.48 | 4.3 | broke at center, origin uncertain |
| | | Average | 0.44 | 3.9 | |
| G-49-1 | 1400°C, 24 hours, partially sealed[6] | 25 | 0.63 | 5.6 | broke at center and end, origin at edge, reddish grey surface |
| G-49-2 | " " " " | 25 | 0.41 | 3.6 | broke at center, origin at edge, reddish gray surface |
| G-49-3 | " " " " | 25 | 0.41 | 3.6 | broke near center, origin near corner, reddish gray surface layer |
| | | Average | 0.48 | 4.3 | |
| G-40-9 | 1400°C, 36-40 hours, partially sealed | 25 | 0.29 | 2.6 | broke near center, origin at or near corner |
| G-40-10 | " " " | 25 | 0.96 | 8.5 | broke near center, origin uncertain, 11 pieces |
| G-40-11 | " " " | 25 | 0.45 | 4.0 | broke at center, origin at edge |
| | | Average | 0.57 | 5.0 | |

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride

(Packed in NUCARB ND 3000, nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-40-12 | 1400°C, 36-40 hours, partially sealed | 1320 | 0.66[5] | 5.8 | broke near center, origin near edge |
| G-40-13 | " " " " | 1320 | 0.76 | 6.7 | broke at center, origin uncertain |
| G-40-14 | " " " " | 1320 | 0.96 | 8.7 | broke near center, origin near surface |
| | | Average | 0.80 | 7.1 | |
| G-48-1 | 1400°C, 40 hours, partially sealed | 25 | 0.42 | 3.7 | broke near center, origin uncertain |
| G-48-2 | " " " " | 25 | 0.35 | 3.1 | broke near center and one end, origin at corner |
| G-48-6 | " " " " | 25 | 0.57 | 5.0 | broke near center and one end, origin at corner |
| | | Average | 0.45 | 3.9 | |
| G-48-3 | 1400°C, 40 hours, partially sealed | 1320 | 0.45[5] | 4.0 | broke at center, origin at corner |
| G-48-4 | " " " " | 1320 | 0.68 | 6.0 | broke at center, origin at edge |
| G-48-5 | " " " " | 1320 | 0.51 | 4.5 | broke near center, origin at or near corner |
| | | Average | 0.55 | 4.8 | |

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride

(Packed in NUCARB ND 3000, nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-38-2 | 1400°C, 48 hours, partially sealed | 25 | 0.50 | 4.4 | edge origin, white spot |
| G-38-3 | " " " " | 25 | 0.47 | 4.2 | corner origin |
| G-38-4 | " " " " | 25 | 0.58 | 5.1 | surface origin |
| | | Average | 0.52 | 4.6 | |
| G-38-6 | 1400°C, 48 hours, oxygen flow | 25 | 0.41 | 3.6 | 2 corner origins, severely oxidized |
| G-38-7 | " " " " | 25 | 0.35 | 3.1 | severely oxidized, origin at pit |
| G-38-8 | " " " " | 25 | 0.72 | 6.4 | severely oxidized, origin at pit |
| | | Average | 0.50 | 4.4 | |
| G-38-10 | 1400°C, 72 hours, completely sealed | 25 | 0.99 | 8.8 | origin at corner |
| G-38-11 | " " " " | 25 | 0.57 | 5.0 | origin at corner |
| G-38-12 | " " " " | 25 | 0.47 | 4.2 | origin at corner |
| | | Average | 0.68 | 6.0 | |

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride

(Packed in NUCARB ND 3000, nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-38-14 | 1400°C, 72 hours, partially sealed | 25 | 0.34 | 3.0 | origin at edge, no branching |
| G-38-15 | " " " " | 25 | 0.33 | 2.9 | origin at or close to corner |
| G-38-16 | " " " " | 25 | 0.31 | 2.7 | origin at corner |
| | | Average | 0.33 | 2.9 | |
| G-40-16 | 1400°C, 72 hours, completely sealed | 25 | 0.32 | 2.8 | broke near center, origin at corner |
| G-40-17 | " " " " | 25 | 0.40 | 3.5 | broke at center, origin at corner |
| G-40-18 | " " " " | 25 | 0.32 | 2.8 | broke near center, origin at edge |
| | | Average | 0.34 | 3.0 | |
| G-40-19 | 1400°C, 72 hours, completely sealed | 1320 | 0.55[5] | 4.9 | broke near center, origin at corner |
| G-40-20 | " " " " | 1320 | 0.50 | 4.4 | broke at center and one end, origin at corner |
| G-40-21 | " " " " | 1320 | 0.68 | 6.0 | broke near center, origin at edge |
| | | Average | 0.58 | 5.1 | |

TABLE XXIV (cont.)

Impact Resistance of Carburized Norton Silicon Nitride
(Packed in NUCARB ND 3000, nominal dimensions 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1,2] Joules | in. lbs | Comments |
|---|---|---|---|---|---|
| G-30-1 | 1450°C, 8 hours, partially sealed | 25 | 0.58 | 5.1 | broke at center, origin at edge loose green surface layer |
| G-30-2 | " " " " | 25 | 0.31 | 2.7 | broke at center, origin at or near corner, loose green surface layer |
| G-30-3 | " " " " | 25 | 0.45 | 4.0 | broke near center, origin uncertain, loose green surface layer |
| | | Average | 0.45 | 3.9 | |
| G-40-2 | 1450°C, 24 hours, partially sealed | 25 | 0.25 | 2.2 | broke near center, origin at edge |
| G-40-3 | " " " " | 25 | 0.32 | 2.8 | broke near center, origin at edge |
| G-40-4 | " " " " | 25 | 0.34 | 3.0 | broke near center, origin at corner |
| | | Average | 0.31 | 2.7 | |
| G-40-5 | 1450, 24 hours, partially sealed | 1320 | 0.33[5] | 2.9 | broke near center, origin at edge |
| G-40-6 | " " " " | 1320 | 0.47 | 4.2 | broke near center, origin at corner |
| G-40-7 | " " " " | 1320 | 0.41 | 3.6 | broke near center, origin at edge |
| | | Average | 0.41 | 3.6 | |

## NOTES FOR TABLE XXIV

(1) One foot pound hammer unless otherwise noted.

(2) Firebrick specimen support used for room temperature tests before experiment G-33. From G-33 onward, the steel support was used. Before experiment G-26, the edges of the specimens were not rounded. From G-26 onward, the edges of the specimens were rounded.

(3) As originally reported these values were twice as high, as were the results for the comparable controls. Available evidence indicates that the original high values occurred as a result of a mistake in reducing the data and that the present results are correct.

(4) Two foot pound hammer.

(5) Graphite - alumina specimen support

(6) Tube broke allowing more air circulation than normal.

The treatment at 1450°C for eight hours (experiment G-30) yielded a small improvement in room temperature impact resistance compared with most groups of controls. However, longer treatments at this temperature resulted in excessive evaporation and no improvement in impact resistance.

Some of the treated specimens had loosely adhering surface layers. These discrete layers may absorb energy during impact, providing another mechanism for improvement of impact resistance.

Subject to some uncertainty because of eratic results attributable to the test method, the best treatment conditions appear to involve temperatures of 1350 or 1400°C and times of 24 to 48 hours.

Flexural strength of carburized Norton silicon nitride

In several experiments the flexural strengths of carburized Norton silicon nitride specimens were measured in further attempts to confirm the strengthening effect of the carburizing treatments. Specimens were cut from the remaining ends of the impact specimens from experiment G-23 (1200°C, 48 hours partially sealed). The flexural strengths of six carburized specimens averaged 511 $MNm^{-2}$ which can be compared with 482 $MNm^{-2}$ for three comparable controls. This difference is probably not significant and, in any case, is not large enough to account for the observed improvement in impact resistance.

In another experiment (G-41) cylindrical rods of Norton silicon nitride were carburized at 1400°C for 24 hours, partially sealed. The flexural strengths of these specimens are presented in Table XXV in which the results are compared with refired controls, and as-machined and polished controls. The carburized specimens were stronger than the refired controls but weaker than the as-machined and polished controls. It is uncertain whether this result reflects only the degree to which the carburizing conditions protect the silicon nitride from degradation or whether there is a strengthening effect.

In still another experiment (G-44), small rectangular bars of Norton NC-132 silicon nitride were carburized at 1400°C for 24 hours, completely sealed and partially sealed. The treated specimens were about 25% stronger than the as-cut controls but all of the results were very low compared with the known flexural strength of Norton silicon nitride. Therefore, it seems likely that machining damage or lack of edge preparation was responsible for these low values. However, the low values cannot be

TABLE XXV

Flexural Strength of Carburized Norton Silicon Nitride

(Cylindrical rods of various diameters)

| Treatment | No. Specimens | Average Flexural Strength(1) $MNm^{-2}$ |
|---|---|---|
| Packed in NUCARB ND 3000, 1400°C, 24 hours, partially sealed | 5 | 597 |
| Refired Controls, 1400°C, 24 hours | 5 | 506 |
| As machined and polished controls | 5 | 708 |

(1) Four point loading on a one inch span

blamed entirely on lack of edge preparation because similar specimens with rounded edges but carburized for 40 hours, partially sealed, had flexural strengths averaging only 574 $MNm^{-2}$, still much lower than expected.

The results of the experiments described above indicate that the Norton silicon nitride is not strengthened significantly by carburization.

Thermal exposure of carburized Norton silicon nitride

Silicon nitride impact bars were carburized by packing in NUCARB ND 3000 at 1400°C for 24 hours, partially sealed, and then exposed at 1315°C for 50 hours in air. The impact resistances of the specimens were measured at room temperature with the results shown in Table XXVI. The carburized specimens were degraded by the 50 hour treatment at 1315°C. This degradation was evident because of the formation of glassy, brown globules on the surface. Pits formed under these globules and in some cases, the fractures were observed to originate at these pits. The pitting was more evident in the case of the second set of experiments compared with the first set and this is consistent with the impact resistance values.

It seems likely that during carburization at 1400°C an appreciable amount of silicon nitride evaporates leaving a residue of impurities on the surface. During thermal exposure at 1315°C these impurities react with the silicon nitride and the air to form the globules and pits.

Two methods of avoiding this difficulty are suggested:

1. Cleaning the surfaces by lapping to remove the impurities before the thermal exposure.
2. Carburization at lower temperatures to reduce the evaporation.

The surfaces of carburized specimens with surfaces cleaned by lapping before thermal exposure were examined after thermal exposure. The appearance of the surfaces was much improved but the pitting was not completely eliminated.

Characterization of carburized Norton silicon nitride

Further efforts were made to characterize the surfaces of Norton silicon nitride specimens carburized by packing in powders.

The surface of a specimen (G-38-10), carburized by packing in NUCARB ND 3000 at 1400°C for 72 hours, completely sealed, was analyzed by x-ray diffraction. The

TABLE XXVI

Impact Resistance of Norton NC-132 Silicon Nitride,
Carburized and Thermally Exposed
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| B-52-1 | Carburized & Thermally exposed | 25 | 0.34 | 3.0 | broke near center, origin at corner, surface glazed & pitted |
| B-52-2 | " " " " | 25 | 0.35 | 3.1 | broke near center, origin at edge, surface glazed & pitted |
| B-52-3 | " " " " | 25 | 0.19 | 1.7 | weak fracture, surface pitted |
| | | Average | 0.29 | 2.6 | |
| B-52-1C | Thermally exposed | 25 | 0.30 | 2.7 | broke near center, origin at edge |
| B-52-2C | " " | 25 | 0.37 | 3.3 | broke near center, origin at edge |
| B-52-3C | " " | 25 | 0.37 | 3.3 | broke near center, origin at edge |
| | | Average | 0.35 | 3.1 | |
| G-52-4 | Carburized & thermally exposed | 25 | 0.18 | 1.6 | - |
| G-52-5 | " " " " | 25 | 0.25 | 2.2 | - |
| G-52-6 | " " " " | 25 | 0.19 | 1.7 | - |
| | | Average | 0.21 | 1.8 | |

TABLE XXVI (cont.)

Impact Resistance of Norton NC-132 Silicon Nitride,
Carburized and Thermally Exposed
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| G-52-1 | Thermally exposed | 25 | 0.42 | 3.7 | - |
| G-52-2 | " " | 25 | 0.32 | 2.8 | - |
| G-52-3 | " " | 25 | 0.38 | 3.4 | - |
| | | Average | 0.37 | 3.3 | |

(1) Steel specimen support, one foot pound hammer

measured impact resistance was 0.99J (8.8 in. lbs.) at room temperature. The diffraction pattern was compared with that of the surface of untreated material. The two patterns are very similar. It is not evident that the treated material contains additional phases. The surface of the treated material appears to be better crystallized and to consist mainly of $\beta$-$Si_3N_4$ and $Si_2ON_2$. The $\beta$-$Si_3N_4$ peaks are shifted to higher angles, perhaps indicating that the unit cell is smaller because of solid solution formation. The unit cell of $Si_2ON_2$ may also be smaller. There is no clear relationship between these observations and the presence of the residual stresses in the treated materials.

The composition profiles near the surface of the same specimen were determined by electron probe microanalysis. The specimen was analyzed for silicon, nitrogen, carbon, aluminum and oxygen. Ideally, the composition of silicon nitride is about 60% silicon and 40% nitrogen, but commercial raw materials contain free silicon, oxygen combined as an oxynitride, and other impurities. In addition, magnesium oxide is usually added to the silicon nitride as a sintering aid and other impurities may be picked up during hot pressing.

The electron beam used for analysis has a substantial width so that the results are averaged over a significant distance during a traverse from one material to another. In the present analysis, the sharpest transitions occurred over 10 to 20 μm. Therefore, transitions over greater distances can be assumed to reflect actual variation in the material, rather than this averaging effect of the electron probe.

The silicon content of the silicon nitride increased gradually to about 50% over a distance of 100-160 μm from the surface. The nitrogen content increases gradually in a similar manner and appears to reach its normal value for the interior of the specimen at about 80 μm from the surface.

The analysis did not detect any unusual concentration of carbon in the surface. The surface and the interior seem to contain about 4% carbon. However, isolated areas higher in carbon were observed in the interior. The width of these areas was about 100-150 μm. The silicon decreased very substantially in these areas, indicating that the carbon probably was not present in a combined form such as silicon carbide (SiC is about 70% silicon). Also, because on a percentage basis the decrease in silicon was

greater than the increase in carbon, it seems likely that other impurities were present in these areas.

Oxygen was uniformly distributed in the specimen, with about 2% present.

The most non-uniform result found during the analysis was the presence of about 2% aluminum concentrated at the surface in a thin layer, perhaps 10 to 40 μm thick. Because the silicon and nitrogen increase gradually over a greater distance, it is likely that other elements, not analyzed, were also concentrated at the surface. The mechanisms by which this concentration occurs are not known, but one mechanism should be considered. It is known that silicon nitride is volatile under these conditions. A rod test specimen treated under similar conditions lost 12% in weight. An impact test specimen, having a lower ratio of surface to volume, would lose less weight proportionately, but the weight loss would still be substantial. If some of the impurities are less volatile than the silicon nitride, as is likely, concentration of impurities at the surface during evaporation of the silicon nitride is reasonable.

The absence of a carbon gradient, the concentration of aluminum at the surface, and peak shifting observed in the silicon nitride by x-ray diffraction analysis combine to indicate that "carburization" does not affect the properties of the ceramic directly by reaction of carbon with the body.

Impact resistance of carburized AVCO silicon nitride

Two types of AVCO silicon nitride were carburized; specimens cut from a billet purchased from AVCO for this program, and specimens from Billet #993 supplied in the form of impact test bars by NASA. When the specimens machined at Ceramic Finishing Company became available, the specimens were included in the experiments being done at the time with Norton silicon nitride. As it turned out, the conditions used for these experiments were not the best possible choices. No obvious improvement resulted from carburization of AVCO material but a better choice of treatment conditions might have given different results. The results of these experiments are reported in Table XXVII.

Test bars supplied by NASA (Billet #993) were carburized in NUCARB ND 3000 at 1400°C for 24 hours, partially sealed. The impact resistance of the carburized and the untreated specimens was measured at room temperature and 1315°C. The results are given in Table XXVIII. The carburizing treatment resulted in a thin black layer on

TABLE XXVII

Impact Resistance of Carburized AVCO Silicon Nitride
(Packed in NUCARB ND 3000, nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Room Temp. Impact Resistance(1) Joules | in. lbs. |
|---|---|---|---|
| G-30-5 | 1450°C, 8 hours, partially sealed | 0.27 | 2.4 |
| G-30-6 | same as above | 0.25 | 2.2 |
| G-30-7 | same as above | 0.29 | 2.6 |
| | Average | 0.27 | 2.4 |
| G-30-12 | 1350°C, 8 hours, partially sealed | 0.35 | 3.1 |
| G-30-13 | same as above | 0.31 | 2.7 |
| G-30-14 | same as above | 0.29 | 2.6 |
| | Average | 0.32 | 3.0 |
| G-31-5 | 1200°C, 48 hours, partially sealed | 0.27 | 2.4 |
| G-31-6 | same as above | 0.28 | 2.5 |
| G-31-7 | same as above | 0.27 | 2.4 |
| | Average | 0.27 | 2.4 |
| G-30-15 | Control | 0.41 | 3.6 |
| G-30-16 | same as above | 0.33 | 2.9 |
| G-30-17 | same as above | 0.35 | 3.1 |
| | Average | 0.37 | 3.2 |

(1) Firebrick specimen support, one foot pound hammer

TABLE XXVIII

Impact Resistance of AVCO Silicon Nitride (Billet #993[1])
(Packed in NUCARB ND 3000, 1400°C, 24 hours, partially sealed, nominal dimension 6.4 x 6.4 x 50.8 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[2] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| 74-159-1 | Carburized | 25 | 0.17[3] | 1.5 | origin at large pore below the surface |
| 74-159-2 | Carburized | 25 | 0.13 | 1.2 | edge origin at small pore on surface |
| | | Average | 0.15 | 1.4 | |
| 74-159-3 | Control | 25 | 0.34[3] | 3.0 | internal origin |
| 74-159-4 | Control | 25 | 0.30 | 2.6 | internal origin |
| | | Average | 0.32 | 2.8 | |
| 74-159-5 | Carburized | 1315 | 0.45[4] | 3.9 | corner origin |
| 74-159-6 | Carburized | 1315 | 0.34 | 3.0 | internal origin |
| | | Average | 0.39 | 3.5 | |
| 74-159-7 | Control | 1315 | 0.44[4] | 3.9 | edge origin |
| 74-159-8 | Control | 1315 | 0.53 | 4.7 | edge origin |
| | | Average | 0.49 | 4.3 | |

(1) Specimens supplied by NASA
(2) One foot pound hammer
(3) Steel specimen support
(4) Graphite - alumina specimen support

the surfaces of the specimens, and pitting occurred on some of the surfaces. The impact measurements at room temperature reflect the presence of the pitting.

Impact resistance of carburized AME reaction bonded silicon nitride

AME reaction sintered $Si_3N_4$ specimens were carburized using four treatments. The results are given in Table XXIX. These results are compared with results for similar material from another lot from which the specimens were fabricated by NASA. No obvious improvement resulted from carburization.

2. Gas carburizing

Two gas carburization experiments were done. In the first of these experiments Norton NC-132 silicon nitride specimens were exposed to benzene at 1400°C for about six hours. During carburization, lampblack, pyrolytic graphite and other carbon deposits were formed on the specimens. These deposits are described in Table XXX. The impact resistances of the specimens were measured and are reported in Table XXXI. These impact resistances seem to be slightly higher than most groups of comparable controls. The rod test results are given in Figure 9. Substantial compressive surface stresses were observed when the specimen was originally slotted at room temperature. As the temperature was increased, the tips of the slot closed, indicating increasing compressive surface stresses. On cooling from 1400°C, the slot width remained essentially unchanged indicating that the high stresses observed at high temperatures were retained on cooling. The increased compressive stress at elevated temperatures may have caused the increased impact resistance at 1315°C.

In the second gas carburization experiment the Norton NC-132 silicon nitride specimens were exposed to two, six hour carburizing treatments. The impact resistances of these specimens were measured and are given in Table XXXII. These results indicate that the impact resistances of the specimens remained essentially unchanged as a result of the treatment. The rod test results are given in Figure 10. Moderate compressive surface stresses were indicated by the slot deflection observed when the specimen was originally slotted. At intermediate temperatures the deflection increased sharply and then decreased at high temperatures. This decrease is less favorable than the behavior illustrated in Figure 9. On cooling to room temperature the slot deflection increased substantially to -.15 mm. This value is close

TABLE XXIX

Impact Resistance of Carburized AME Reaction Sintered Silicon Nitride

(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Room Temp. Impact Resistance[1] Joules | in. lbs. |
|---|---|---|---|
| G-25-7 | Packed in NUCARB ND 3000, 1200°C, 20 hours, completely sealed | 0.057 | 0.5 |
| G-25-8 | same as above | 0.10 | 0.9 |
| G-25-9 | same as above | 0.12 | 1.1 |
| | Average | 0.09 | 0.8 |
| G-25-10 | Packed in NUCARB ND 3000, 1200°C, 20 hours, partially sealed | 0.08 | 0.7 |
| G-25-11 | same as above | 0.31(?) | 2.7(?) |
| G-25-12 | same as above | 0.057 | 0.5 |
| | Average | - | - |
| G-25-13 | Packed in NUCARB ND 3000, 1200°C, 48 hours, completely sealed | 0.11 | 1.0 |
| G-25-14 | same as above | 0.12 | 1.1 |
| G-25-15 | same as above | 0.09 | 0.8 |
| | Average | 0.11 | 1.0 |
| G-25-16 | Packed in NUCARB ND 3000, 1200°C, 48 hours, partially sealed | 0.18 | 1.6 |
| G-25-17 | same as above | 0.12 | 1.1 |
| G-25-18 | same as above | 0.08 | 0.7 |
| | Average | 0.13 | 1.1 |

TABLE XXIX (Cont.)

Impact Resistance of Carburized AME
Reaction Sintered Silicon Nitride
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Room Temp. Impact Resistance[1] Joules | in. lbs. |
|---|---|---|---|
| - | Control | 0.14 | 1.2 |
| - | Control | 0.15 | 1.3 |
| | Average | 0.15 | 1.3 |

(1) Firebrick specimen support, one foot pound hammer

TABLE XXX

Surface Deposits on Norton NC-132 Silicon Nitride
Gas carburized at 1400°C for 6 hours

| Gas Flow | Specimen No. | Description |
|---|---|---|
| ↑ | 1 | Lamp black, and whiskers |
| | 2 | Lamp black,and whiskers |
| | 3 | Lamp black, some whiskers, and small amount of pyrolitic graphite |
| | 4 | Lamp black, pyrolitic graphite, and small amount of whiskers (apparently amorphous) |
| | 5 | Pyrolitic graphite(1), and lamp black |
| | 6 | Pyrolitic graphite(1), and small amount of lamp black |

(1) Pyrolitic graphite blistered and peeled in small areas.

TABLE XXXI

Impact Resistance of Norton NC-132 Silicon Nitride
Gas carburized at 1400°C for 6 hours
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|
| 74-155-1 | 25 | 0.69[2] | 6.1 | broke near center, origin near corner, 11 pieces |
| 74-155-3 | 25 | 0.35 | 3.1 | broke at center, origin at corner |
| 74-155-5 | 25 | 0.23 | 2.1 | broke near center, origin at edge |
| | Average | 0.42 | 3.8 | |
| 74-155-2 | 1320 | 0.83[3] | 7.3 | broke at center, origin at edge |
| 74-155-4 | 1320 | 0.65 | 5.7 | broke at center, origin at corner |
| 74-155-6 | 1320 | 0.76 | 6.8 | broke at center, origin at corner |
| | Average | 0.75 | 6.6 | |

(1) One foot pound hammer

(2) Steel specimen support

(3) graphite - alumina specimen support

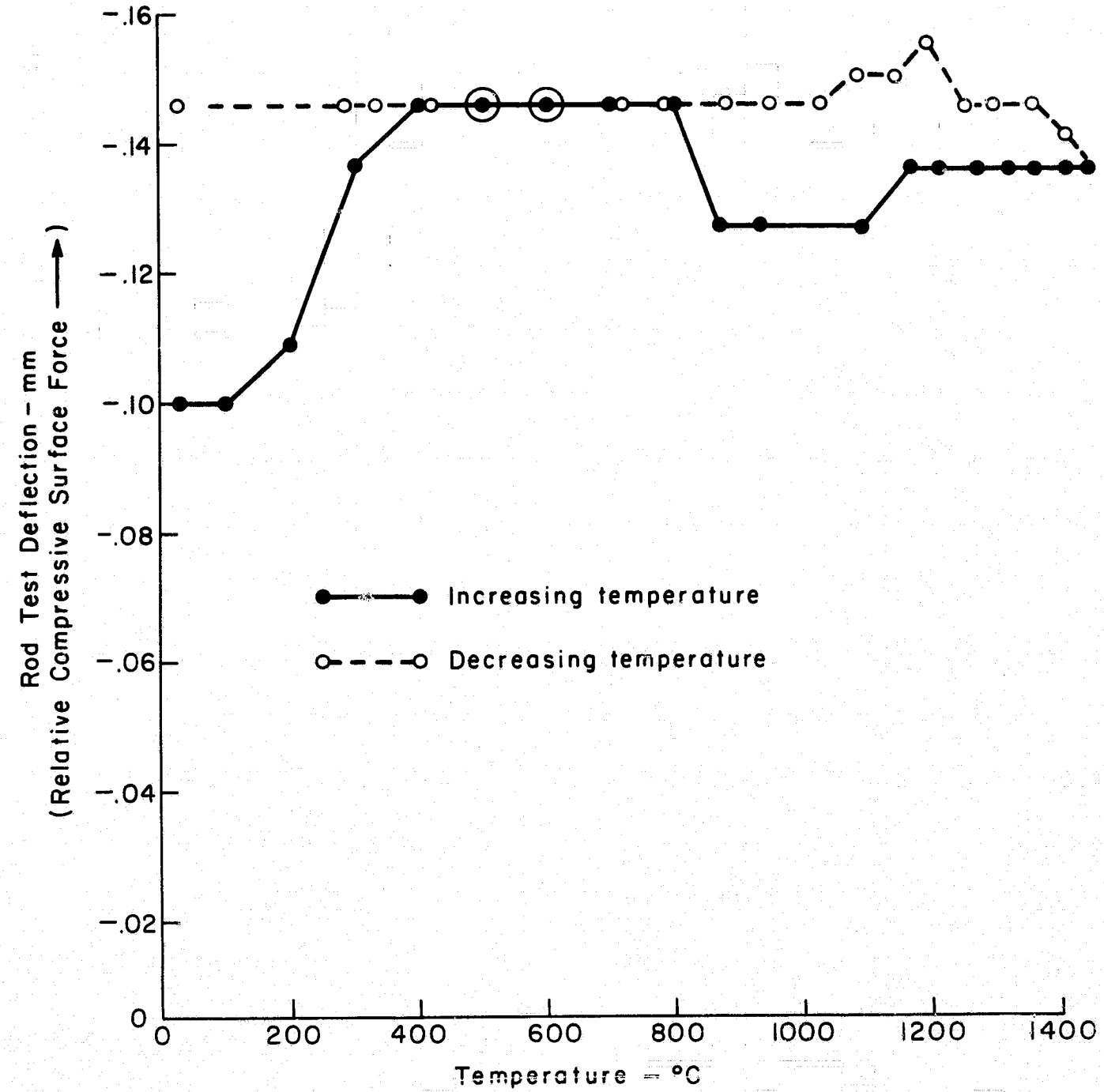



Figure 9 Elevated temperature rod test, Norton NC-132 silicon nitride, carburized with benzene, 1400 °C, 6 hours.

TABLE XXXII

Impact Resistance of Norton NC-132 Silicon Nitride
Gas carburized at 1400°C for two, six-hour cycles
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|
| 74-161-1 | 25 | 0.45[2] | 4.0 | broke at center, origin at corner, uneven white surface |
| 74-161-3 | 25 | 0.33 | 3.0 | broke near center, origin at edge |
| 74-161-5 | 25 | 0.28 | 2.5 | broke near center, origin at edge, loose gray patches on surface |
| | Average | 0.35 | 3.1 | |
| 74-161-2 | 1315 | 0.33[3] | 2.9 | broke near center, origin at edge, gray and white surface discoloration |
| 74-161-4 | 1315 | 0.29 | 2.6 | broke at center, origin at edge, surface discoloration |
| 74-161-6 | 1315 | 0.59 | 5.3[4] | broke near center, origin at corner, bumpy corroded surface |
| | Average | 0.41 | 3.6 | |

(1) One foot pound hammer
(2) Steel specimen support
(3) Graphite - alumina specimen support
(4) No failure on first impact, failure on second impact

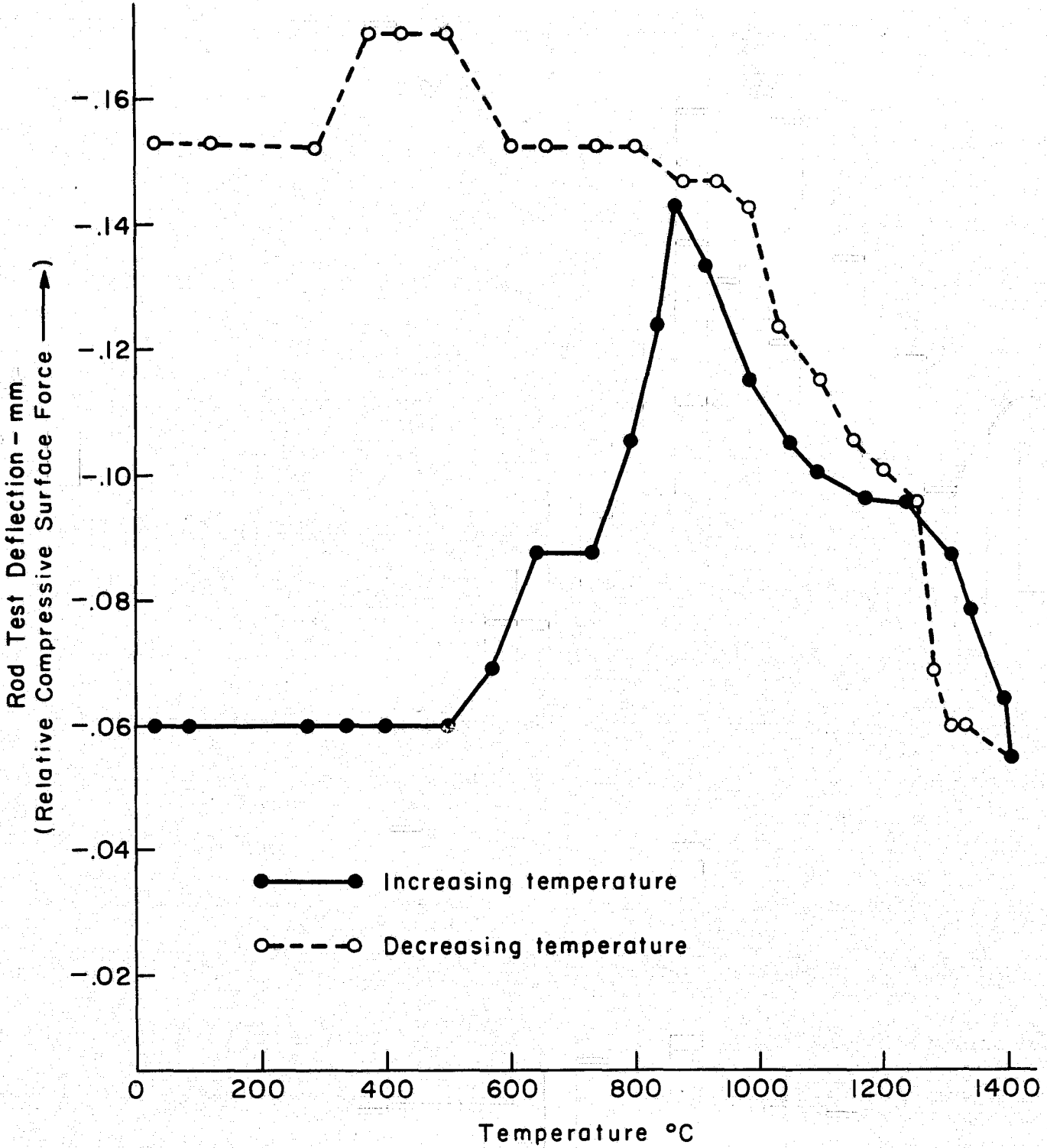



Figure 10 Elevated temperature rod test, Norton NC-132 silicon nitride, carburized with benzene, 1400 °C, two - 6 hour cycles.

C. 2

to that obtained for the other specimen (6 hour treatment) after cooling to room temperature. The surface of a specimen subjected to two six-hour gas carburization treatments was examined by X-ray diffraction. The diffraction pattern was completely different from that obtained from specimens carburized by packing, especially because of the strong pattern of $\alpha$-$SiO_2$ (low cristobalite) and unidentified phases.

The rod test results obtained in the gas carburization experiments seem to be especially promising because of the high compressive stresses indicated by the tests. Also, in the case of the specimens receiving one six-hour treatment, the impact resistances were high at 1315°C. Therefore, gas carburization should be the subject of further investigation.

F. Carburizing and quenching of silicon nitride

An obvious approach to obtain further improvements in impact resistance is to combine two or more treatments that separately are effective. However, the best way to combine the processes is far from obvious.

As a first step toward learning how to combine these treatments, Norton NC-132 silicon nitride specimens were carburized by packing in NUCARB ND 3000 at 1400°C for 24 hours, partially sealed. After cooling to room temperature, unpacking, and cleaning in methanol, the specimens were reheated to 1350°C and quenched into silicone oil (50 cSt.).

The impact resistances of the specimens were measured and are given in Table XXXIII. At room temperature, the impact resistances of the specimens that were carburized and quenched were lower than those that were only quenched. At 1315°C, the measured impact resistances were very high. In two cases, the specimens did not break on the first impact, and then when they did break on the second impact, nigh values were obtained. After the second time this occurred, the alumina specimen support rod was found to be tilted to one side. Further examination showed that it was broken down inside the graphite susceptor. This support rod may have cracked during the earlier tests. This may account for the fact that in two cases the specimens did not fracture on the first impact and yielded high values on the second impact.

TABLE XXXIII

Impact Resistance of Norton NC-132 Silicon Nitride

Carburized at 1400°C for 24 hours
Quenched from 1350°C into 50 cSt. Silicone Oil
(Nominal dimension 6.4 x 6.4 x 57.2 mm.)

| Specimen No. | Treatment | Test Temp. °C | Impact Resistance[1] Joules | in. lbs. | Comments |
|---|---|---|---|---|---|
| 74-164-1 | Carburized & Quenched | 25 | 0.38[2] | 3.4 | broke near center, origin at corner |
| 74-164-2 | same as above | 25 | 0.48 | 4.3 | broke new center, origin at edge |
| 74-164-3 | same as above | 25 | 0.36 | 3.2 | broke near center, origin at edge |
| | | Average | 0.41 | 3.6 | |
| 74-164-4 | Quenched | 25 | 0.75[2] | 6.6 | broke near center, origin near edge, 7 pieces |
| 74-164-5 | same as above | 25 | 0.39 | 3.5 | broke at center, origin at corner |
| | | Average | 0.57 | 5.1 | |
| 74-164-6 | Carburized & Quenched | 1315 | 1.07[3] | 9.5[4] | broke near center and one end, origin at corner, 8 pieces |
| 74-164-7 | same as above | 1315 | 0.90 | 8.0[4] | [5] broke near center, origin at edge |
| 74-164-8 | same as above | 1315 | 0.66 | 5.8 | broke near center, origin at corner |
| | | Average | 0.87 | 7.8 | |

(1) One foot pound hammer
(2) Steel specimen support
(3) Graphite - alumina specimen support
(4) No failure on first impact, failure on second impact
(5) Alumina specimen support rod broke during second impact

# V. CONCLUSIONS

In this investigation silicon carbide and silicon nitride ceramics were treated to form compressive surface layers. Impact resistance, flexural strength, and slotted rod tests were used to evaluate the treated specimens. The results of the various treatments were as follows:

## Quenching of silicon carbide

The difficulties with thermal shock cracks, previously encountered during quenching of standard impact test specimens, were overcome by quenching from 2000°C into a $ZrO_2$-air fluidized bed at room temperature. The presence of compressive surface stresses was demonstrated by rod tests. Improvements in impact resistance were observed for several groups of specimens, both at room temperature and at 1320°C. The room temperature flexural strength was also improved.

## Thermal exposure of silicon carbide

Thermal exposure (1315°C for 50 hours in air) of Norton hot pressed silicon carbide resulted in a substantial improvement in impact resistance. Although crack healing in silicon carbide is well known, the improvements in flexural strength of hot pressed silicon carbide observed by Lange[19] were only 5 to 10% after heating for 96 hours at 1400°C. Therefore, the present improvement in impact resistance cannot be accounted for entirely on the basis of crack healing and evidence for other mechanisms is lacking.

## Quenching of silicon nitride

Contrary to expectations, the best quenching temperatures for hot pressed silicon nitride were relatively low temperatures such as 1350 or 1400°C. The flexural strengths of specimens quenched from 1350°C into 50 cSt. silicone oil were increased by as much as 30%. The room temperature impact resistance was also improved. Present evidence indicates that the major part of the improvement is attributable to a mechanism such as flaw healing that does not depend on quenching and that a minor part is attributable to compressive surface stresses.

## Carburizing of silicon nitride

Presently available evidence indicates that the best conditions for carburizing by packing involve treating at 1400°C for periods of 24 to 48 hours. Higher temperatures and longer treatment times lead to excessive evaporation. Slotted rod tests demonstrated the presence of compressive surface stresses at room temperature and at elevated temperatures to 1400°C. The mechanism by which these stresses occur is not understood. Substantial improvements in impact resistance were observed for several groups of carburized silicon nitride specimens.

Gas carburization resulted in compressive surface stresses at room temperature and at elevated temperatures to 1400°C. Further investigation of gas carburization is recommended.

## Carburizing and quenching of silicon nitride

Carburized silicon nitride specimens were quenched from 1350°C into 50 cSt. siliconeoil and the impact resistances were measured. Because the results were confused to some extent by testing problems, it is uncertain whether or not the combined processes resulted in further improvement in impact resistance.

## Assessment of improvements in relation to practical applications

Compressive surface stresses can be used to improve the tensile strength, flexural strength, delayed fracture performance and resistance to thermal shock, impact and penetration of surface damage of ceramic materials. All of these properties will be of considerable importance for application of ceramics in gas turbines. Other mechanisms, such as the use of energy absorbing surface layers to improve impact resistance, provide substantial improvements. By combining treatments to obtain energy absorbing surface layers and compressive surface stresses further improvements in properties are likely.

The use of combined proof testing and fracture mechanics methods for failure prediction[20, 21] indicate gloomy prospects for the use of ceramics in critical applications unless something drastic can be done that will radically alter the predicted times to failure. There are several reasons for this including the fact that high overload proof test ratios are necessary to assure reliability so only a small fraction of the measured strength can be used, or alternatively many components must be tested and destroyed to find the few that have small flaws. One means to drastically alter the situation is to strengthen the components by compressive surface stresses. This method will permit proof

testing at much higher stresses without losing a substantial number of components and will lead to substantial increases in service life. In one investigation use of compressive surface stresses resulted in predicted improvements in service life of alumina ceramics of about 15 ordersof magnitude[22].

Recent research indicates that the impact resistance of ceramics depends primarily on elastic deflection energy which increases as the square of the fracture stress[17]. Therefore, improvements in strength can yield substantial improvements in impact resistance.

The methods used in this investigation can yield further improvements in mechanical properties of materials for gas turbine applications. Additional research is needed to demonstrate these improvements. This additional research should include further improvements in the individual processes. The results achieved in treating alumina ceramics and glass which have been the subjects of more extensive investigations can be used to estimate the potential for further improvements of these processes. It should also include further investigation of combined processes and evaluation of treated components.

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