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EFFECT OF W AND WC ON THE OXIDATION RESISTANCE OF YTTRIA-DOPED SILICON NITRIDE

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ERRATA

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ABSTRACT

The effect of W and WC contamination on the oxidation and cracking in air of sintered Si_3N_4 - 8 w/o Y_2O_3 ceramics was studied at 500°, 750°, and 1350° C. A mixture of Si_3N_4 - 8 Y_2O_3, milled with alumina balls, was divided into four portions. Three portions were doped with 2 w/o WC, 2 w/o W, and 4 w/o W respectively, in order to simulate contamination during milling. The fourth portion was undoped and used on a control. The addition of W or of WC did not affect the phase relationships in the system, as all bars with or without additions contained melilite as the major Si-Y-O-N phase after sintering.

At 750° C, instability (rapid oxidation and cracking) of W-doped bars appears to have occurred as a result of oxidation of the tungsten-containing melilite phase. No intermediate temperature instability was observed in bars containing 2 w/o WC or in bars with no additive. Specimens exposed at 1350° C had good oxidation resistance due to the formation of a protective siliceous oxide layer. A specimen containing 4 w/o W which was pre-oxidized at 1350° C had improved oxidation resistance at 750° C.

The tendency towards oxidation and cracking of Si_3N_4-8Y_2O_3 at 750° C is concluded to be related to tungsten content of the sintered bars.

INTRODUCTION

Yttria-doped silicon nitride is a promising material for high temperature applications. Unlike MgO-doped silicon nitride, yttria-doped silicon nitride has good flexural strength and creep rupture strength above 1200° C.[1] Although high temperature flexural strength was found to increase with increasing yttria content, severe degradation in mechanical properties has been observed at intermediate temperatures (approx. 1000° C) with yttria contents greater than 8 percent.[2] Therefore, material containing 8 percent yttria, was developed as an optimized material.[1] However, some batches of NCX-34*, a commercial hot-pressed material containing nominally 8 percent yttria have been observed to deteriorate catastrophically at intermediate temperatures, 600° to 900° C.[3]

Tungsten carbide is often present in commercial yttria-doped silicon nitride if the powder is milled with WC balls.[4] Approximately 1 to 3 percent WC can be introduced into the powder in this manner (J. Brennan, Norton Co., personal communication). Free carbon which forms during the decomposition of tungsten carbide during sintering or from hydrocarbon contamination

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*Norton Co.

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during milling most likely forms silicon carbide during sintering or is volatilized as CO[5]. Tungsten carbide and silicon carbide are common phases in commercial hot-pressed Si_3N_4. Although tungsten carbide is present in MgO-doped Si_3N_4, such as HS-130** and NC-132**, catastrophic oxidation is not observed in these materials.[6] In this study, the role of tungsten in the oxidation resistance of yttria-doped silicon nitride was investigated to determine whether it might be contributing to the oxidation problem observed in materials such as NCX-34.

EXPERIMENTAL

In order to minimize variability between specimens, dopants were mixed with silicon nitride powder in two stages:

1. Initially, 8 wt. percent yttria was added to CP 85 silicon nitride powder*** and milled with ethanol for 16 hours in a polyethylene bottle using Al_2O_3 balls. The resultant slurry was dried and sieved through a 60 mesh screen.
2. The powder was then divided into four equal lots for the addition of dopants (2 w/o W, 4 w/o W, 2 w/o WC, and one lot without an additive). Each doped mixture was further milled for two hours with ethanol in a polyethelene bottle using Al_2O_3 balls. The slurries were dried and sieved through a 60 mesh screen.

The powder mixtures were cold pressed without a binder in a single acting die followed by isostatically cold pressing in rubber sleeves at a total pressure of 483 MPa. The bars (7.3x1.2x1.2 cm) from all four mixtures were sintered in the same furnace run on reaction bonded silicon nitride plates for three hours at 1750° C. This sintering was done in flowing nitrogen in a furnace with tungsten heating elements. The sintered bars had a density of about 2.1 gm/cc compared with a density of about 3.2 gm/cc for NCX-34.

Specimens 1.0x0.5x0.5 cm and 1.0x1.0x0.5 cm were machined from the sintered bars. The specimens were placed on reaction bonded silicon nitride plates and exposed in air at 500°, 750° and 1350° C for various lengths of time.

For oxidation tests, the furnace was brought up to temperature before the specimens were placed into the furnace. Specimens were taken from the furnace at different time intervals, cooled in air to room temperature and weighed, and then returned to the furnace for continued exposure. One specimen containing 4 w/o W was preoxidized at 1350° C for 20 hours, removed from the furnace and reexposed at 750° C for 20 and for 450 hours.

After oxidation, the test specimens were studied by scanning electron and optical microscopy. Phase determinations were made by X-ray diffraction.

RESULTS AND DISCUSSION

As-sintered bars of all four compositions had very similar microstructures and phase compositions. The microstructures of the as-sintered bars were

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**Norton Co. (MgO doped, hot-pressed Si_3N_4)

***Kawecki Berylco (85% α-Si_3N_4, 15% β-Si_3N_4, particle size range of 0.05 to 6 μm) heterogeneous. Regions of high density, darker gray regions in Figure 1, had high concentrations of trace elements (Ca, Ti and Fe) as determined by STEM analysis. Yttrium was also concentrated in the high density regions. A bimodal distribution of grain size was revealed by TEM. Finer grains occur in dense regions whereas courser grains were observed in the porous regions. X-ray analyses of sintered bars revealed β-Si_3N_4, n-melilite ($Si_3Y_2O_3N_4$), an amorphous phase, and a minor amount of α-Si_3N_4. W_5Si_3 was found in sintered bars doped with 2 w/o W and 4 w/o W. Determination of tungsten carbide and other tungsten and yttrium-containing phases was impossible due to interference from other phases and their very low concentrations. Elemental tungsten was not observed as a secondary phase.

At 500° C, only minor oxidation was observed. The plots of weight gain versus exposure time indicate that the oxidation resistance of the as-sintered specimens decreased with increasing tungsten content Figure 2. No cracking was observed in any specimen.

At 750° C, instability was observed in specimens containing 2 and 4 w/o W. As can be seen in Figure 3, the rates of oxidation for specimens contaning 2 w/o WC and no additive were low in comparison to the rates for specimens containing 2 w/o W and 4 w/o W. The rate of oxidation was greatest for specimens containing 4 w/o W. Instability was observed in bars containing 4 w/o W after only one hour. As shown in Figure 4, the 2 W w/o specimen was cracked and the 4 w/o specimen had crumbled after exposure for 20 hours. Catastrophic oxidation was not observed in undoped Si_3N_4 - 8 Y_2O_3 nor in specimens with 2 w/o WC. As oxidation proceeded, the specimens deteriorated further until only coarse grains were left as shown in Figure 5. X-ray analysis revealed only β-Si_3N_4 and a minor amount of amorphous phase after catastrophic oxidation of specimens containing 2 w/o W and 4 w/o W. No metilite was observed.

At 1350° C, all materials formed a protective oxide layer, shown in Figure 6. X-ray analysis showed the oxide layer to be principally cristobolite and an amorphous phase. This oxide layer apparently formed rapidly and tended to seal the surface from further oxidation as shown in Figure 7. As shown in Figure 8 all compositions gained weight rapidly during the first hour of oxidation and later gained weight slowly. No cracking was observed in any of these bars after 20 hours exposure. In contrast to specimens oxidized at 500° and 750° C, the 1350° C specimens containing 2 w/o WC gained less weight than specimens with no additive.

In an attempt to improve oxidation behavior at intermediate temperatures, specimens doped with 4 w/o W were pre-oxidized for 20 hours at 1350° C and then exposed at 750° C. Considerable improvement was observed relative to the behavior of non-pre-oxidized specimens in oxidation resistance. Whereas, [illegible]-oxidized material crumbled to a powder in less than two hours at 750° C, material pre-oxidized at 1350° C cracked after 20 hours exposure at 750° C as shown in Figure 9. No further degradation of the pre-oxidized 4 w/o material was apparent after over 450 hours exposure at 750° C.

For a given composition, the rate of oxidation appears to vary with the porosity of the ceramic bar. As-sintered surfaces, which were more porous than the interior of the bars, oxidized faster at 750° C than machined surfaces, as shown in Figure 10. Severe cracking and volume expansion also first occurred at as-sintered surfaces. Although accelerated surface oxidation has been attributed to the presence of carbon as the result of a reaction between the sample and a graphite die,[4] this could not have been a factor in this study because bars were not sintered in a carbonaceous atmosphere. Moreover, carbon and tungsten carbide introduced prior to sintering would have been uniformly distributed during milling. Therefore, we attribute the more rapid oxidation of the unmachined surface (Fig. 10) to the greater porosity of the as-sintered surfaces.

Impurities are easily introduced in the manufacture of Si_3N_4 powder and during processing. As pointed earlier, commercial powders are often milled in ethanol using tungsten carbide balls thereby introducing both tungsten and carbon.[4] Tungsten carbide is thus a frequent impurity in commercial yttria doped Si_3N_4 such as NCX-34. Tungsten may be present as a minor phase (W_5Si_3 or WC)[6] or in solution in a Si-Y-O-N grain-boundary phase. If tungsten carbide decomposed at high hot-pressing temperatures, tungsten could enter either the glass structure or the crystal structure of a Si-Y-O-N phase. The major Si-Y-O-N phase in the sintered bars in this study was n-melilite ($Si_3Y_2O_3N_4$). This phase has been considered to be isostructural with akermanite ($Ca_2MgSi_2O_7$), a member of the melilite silicates.[7] Si-O-N tetrahedra form layers normal to the c-axis of the melilite structure. In akermanite, Ca and Mg cations occupy sites between layers. In $Si_3Y_2O_3N_4$, Y ions (9.2×10^{-11}m) replace Ca ions (9.9×10^{-11}m) in the melilite structure. It is also likely that W (6.2×10^{-11}m) could easily substitute for Mg (6.6×10^{-11}m) as they are similar in size.

We suggest that tungsten substitution into the lattice structure causes instability in the melilite phase, which is normally considered metastable in Si_3N_4-8 Y_2O_3.[8] The decomposition of melilite could then, through volume changes, cause the cracking and rapid oxidation which occurs at intermediate temperatures. This suggestion is consistent with our observations that only undoped and WC-doped Si_3N_4-8 Y_2O_3, which showed minimal oxidation at 750° C, contained melilite after the 750° C exposure.

We interpret the results of the present study as strongly suggesting that tungsten contamination from WC grinding balls may be the major cause of the intermediate temperature cracking and accelerated oxidation frequently observed in Si_3N_4-8 Y_2O_3.

SUMMARY OF RESULTS

The effects of W and WC contamination on the oxidation in air of sintered Si_3N_4 - 8 w/o Y_2O_3 ceramics was studied at 500°, 750°, and 1350° C. The results can be summarized as follows:

1. The addition of 2 w/o and 4 w/o W and 2 w/o WC did not affect the phase relationships in as-sintered bars. All bars, regardless of W or WC content were composed of α-Si_3N_4, β-Si_3N_4, melilite, and an amorphous phase.
2. At 750° C, catastrophic oxidation occurred during air exposure of specimens containing 2 and 4 w/o W. Specimens doped with 2 w/o WC and those without additive showed only small weight gains at 750° C.
3. After catastrophic oxidation of W-doped specimens at 750° C, only β-Si_3N_4 and a minor amount of amorphous phase remained. Melilite was not detected in these specimens.
4. At 1350° C, a protective glassy oxide layer formed on all specimens. Catastrophic oxidation of specimens doped with W was not observed.
5. Pre-oxidation at 1350° C to form a protective oxide improved the oxidation resistance at 750° C of bars doped with 4 w/o W.
6. Tungsten contamination may be the major cause of intermediate temperature cracking and instability in Si_3N_4-8Y_2O_3.

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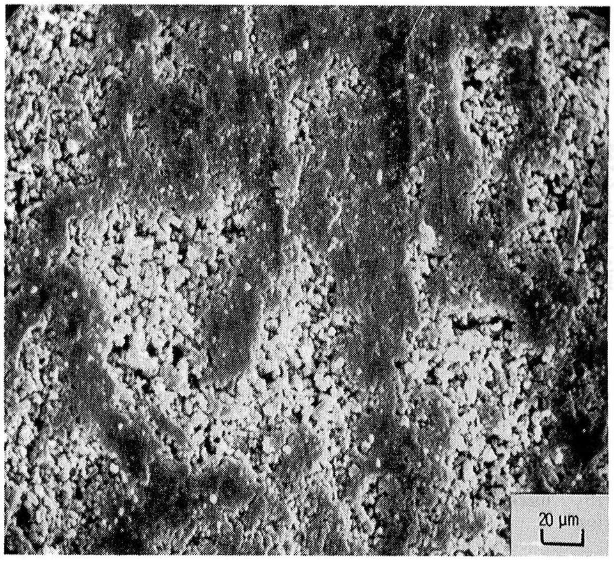

Figure 1. - SEM micrograph of the machined surface of sintered Si_3N_4 + 8 w/o Y_2O_3 doped with 2 w/o WC.

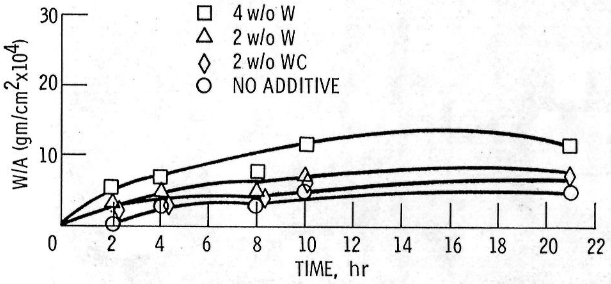

Figure 2. - Weight gain of various $Si_3N_4 \cdot Y_2O_3$ compositions oxidized in air at 500° C as a function of exposure time.

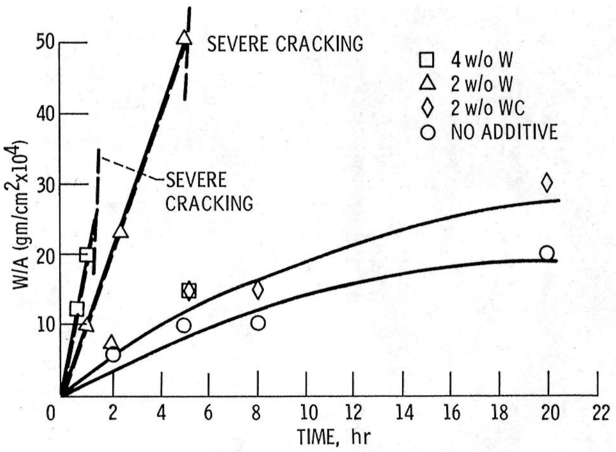

Figure 3. - Weight gain of various $Si_3N_4 \cdot Y_3O_4$ compositions oxidized in air at 750° C as a function of exposure time.

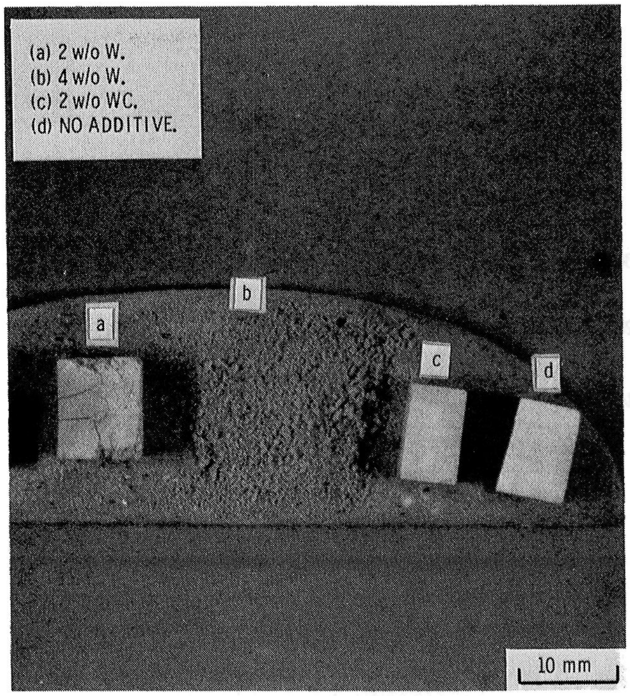

Figure 4. - Various Si_3N_4 + 8 w/o Y_2O_3 compositions oxidized for 20 hours at 750° C.

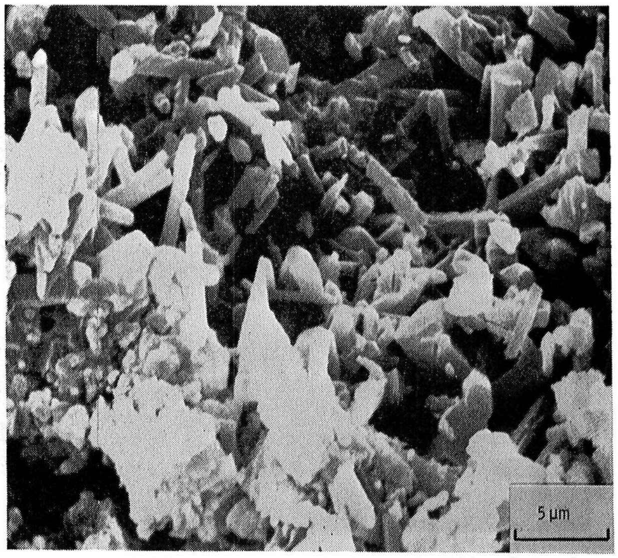

Figure 5. - SEM micrograph of the machined surface of sintered Si_3N_4 + 8 w/o Y_2O_3 doped with 2 w/o W oxidized in air at 750° C for 20 hours showing coarse-grained structure.

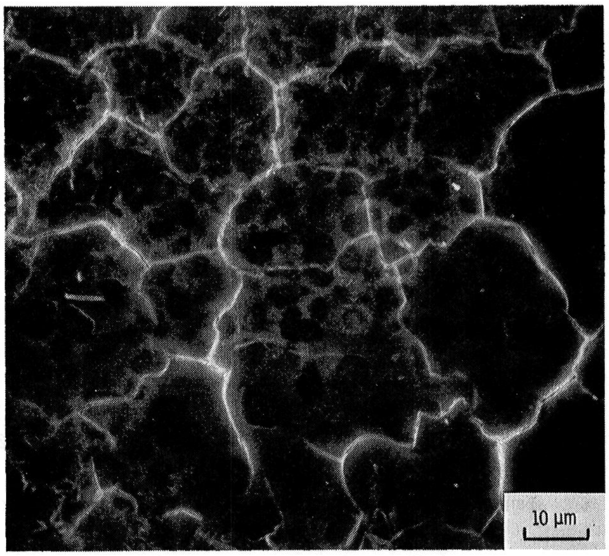

Figure 6. - SEM micrograph of the machined surface of sintered Si_3N_4 + 8 w/o Y_2O_3 doped with 4 w/o W oxidized in air at 1350° C for 20 hours showing a protective oxide layer.

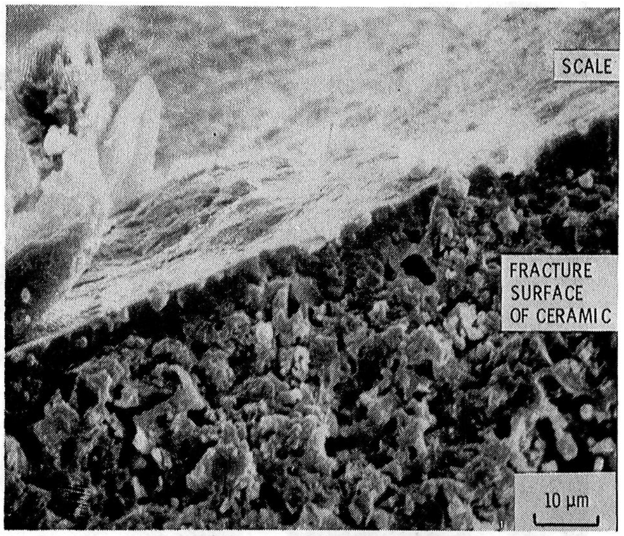

Figure 7. - SEM micrograph of a cross section of sintered Si_3N_4+ w/o Y_2O_3 doped with 4 w/o W, oxidized in air at 1350° C for 20 hours showing a protective oxide layer on the surface of the specimen.

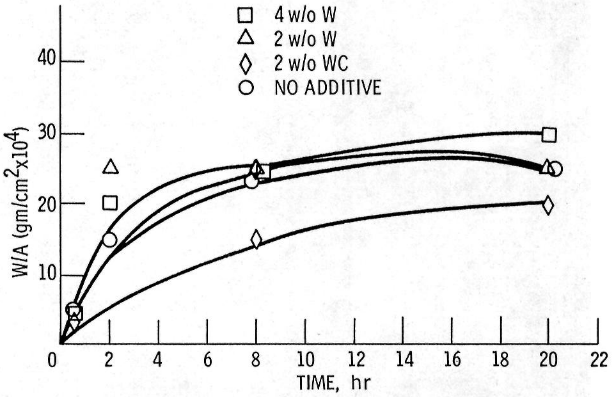

Figure 8. - Weight gain of various $Si_3N_4 \cdot Y_2O_3$ compositions oxidized in air at 1350° C as a function of exposure time.

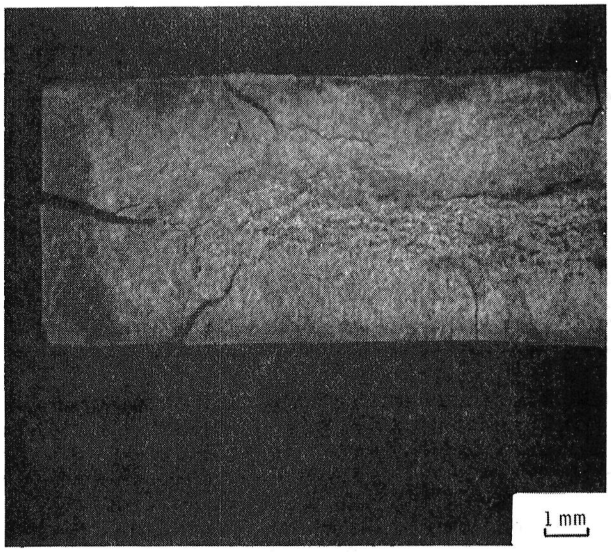

Figure 9. - Sintered Si_3N_4 + 8 w/o Y_2O_3 doped with 4 w/o W preoxidized at 1350° C for 20 hours and exposed for 20 hours at 750° C (machined surface on top and bottom of specimen, as-sintered surface on left side of specimen, fractured after oxidation).

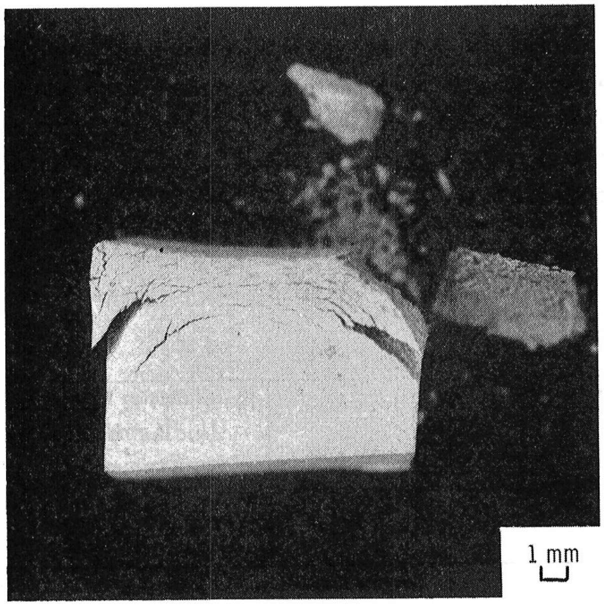

Figure 10. - Sintered Si_3N_4 + 8 w/o Y_2O_3 doped with 2 w/o W oxidized in air at 750° C for 20 hours. (As-sintered face on top, machined face on bottom.)

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15. Supplementary Notes

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16. Abstract

The effect of W and WC contamination on the oxidation and cracking in air of sintered Si_3N_4 - 8 w/o Y_2O_3 ceramics was studied at 500°, 750°, and 1350° C. A mixture of Si_3N_4 - 8 Y_2O_3, milled with alumina balls, was divided into four portions. Three portions were doped with 2 w/o WC, 2 w/o W, and 4 w/o W respectively, in order to simulate contamination during milling. The fourth portion was undoped and used on a control. The addition of W or of WC did not affect the phase relationships in the system, as all bars with or without additions contained melilite as the major Si-Y-O-N phase after sintering. At 750° C, instability (rapid oxidation and cracking) of W-doped bars appears to have occurred as a result of oxidation of the tungsten-containing melilite phase. No intermediate temperature instability was observed in bars containing 2 w/o WC or in bars with no additive. Specimens exposed at 1350° C had good oxidation resistance due to the formation of a protective siliceous oxide layer. A specimen containing 4 w/o W which was preoxidized at 1350° C had improved oxidation resistance at 750° C. The tendency towards oxidation and cracking of Si_3N_4 - 8 Y_2O_3 at 750° C is concluded to be related to tungsten content of the sintered bars.

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