Anomalous Ultra-small-angle X-ray Scattering From Voids and Secondary Phases As a Function of Ceramic Deformation

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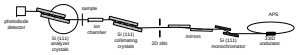
Abstract

Creep cavitation is one of the principal factors limiting the use of silicon nitride in high temperature applications. Recently, it has been shown that its performance can be improved significantly by adding a refractory crystalline secondary phase and residual glass with high softening temperature. High creep resistance appears to result from the new types of sintering additives. This research was undertaken to explore the limits of creep performance of next generation silicon nitride by measuring the void population and the secondary phase population as a function of deformation.

Ultra-small-angle X-ray scattering provides quantitative and statistically significant data on the size distribution of electron density inhomogeneities between 6 nm and 5 µm. A single scattering curve, however, includes information on all of the scatterers, making it difficult to distinguish overlapping populations. In particular, the rare earth oxy-nitride additives and the creep cavities possess similar scattering contrast and are practically identical in size. Anomalous-USAXS offers an opportunity to vary the scattering contributions from one population while holding that of the others fixed. Knowledge of how each of these populations evolves as a function of high-temperature deformation is crucial for understanding the deformation process and for developing better ceramics. We show a-USAXS results on the evolution of both the oxy-nitrides and the cavities in tensile-crept commercial silicon nitrides.

UNICAT USAXS instrument at beam line 33ID, APS



- APS undulator A
- X-ray energy tunability: 7 – 11 keV (to date)
- energy resolution: ΔE/E = 0.00015
- harmonic rejection > 10^{-6}
- sample in air
- 0.6 x 1.6 mm^2 beam size
- Q range: $0.00015 \le Q, Å^{-1} \le 0.5$
- absolute determination of $d\Sigma/d\Omega(Q)$

A-USAXS, the basics

scattering vector magnitude $Q = (4\pi/\lambda)\sin\theta$

intensity of scattering $I(Q) = \frac{d\Sigma}{d\Omega}(Q,E) = \sum_k |\Delta\rho_k(E)|^2 \int_0^\infty N_k(D) V^2(D) |F(Q,D)|^2 \, dD$

intensity, simplified $I(Q,E) = \int_0^\infty \varphi(D,E)\, G(Q,D)\, dD$

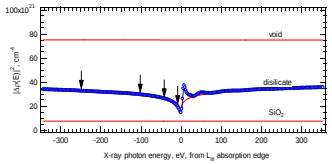
Use scattering contrast to separate *f(D)* for each population $\varphi(D,E) = |\Delta\rho_{disilicate}(E)|^2 \, f_{disilicate}(D) + |\Delta\rho_{void}|^2 \, f_{void}(D)$

determination of creep cavity population $f_{creep\text{-}cavities}(D) = f_{void,gage}(D) - f_{void,grip}(D)$

Background

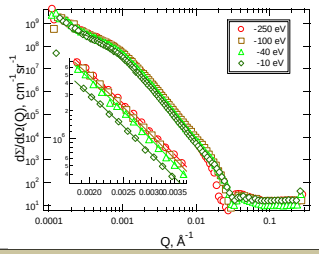
- Silicon nitride
- Prime candidate for structural components in advance gas turbines at high turbine inlet temperatures
- Creep compromises excellent high-temperature mechanical proerties
- Cavitation possibly most important mechanism resulting in creep deformation
- Earlier USAXS showed deformation occurs via cavity accumulation at multigrain junctions
- Evolution of secondary phase pockets not yet studied due to lack of suitable technique
- A-USAXS to follow evolution of Yb-rich secondary phase and voids with creep testing

X-ray scattering contrast of scatterers in SN-88 near the Yb L_{III} edge

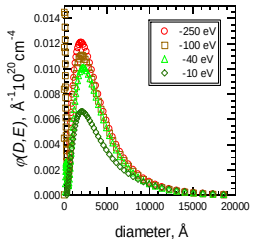


$$\Delta\rho_k(E) = r_e(E)\sum_x \Delta c_{Z_x}\left[Z + f_Z'(E) + if_Z''(E)\right]$$

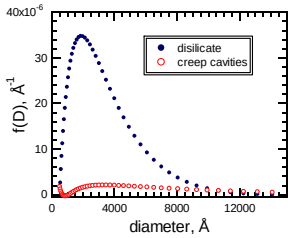
A-USAXS near the Yb L_{III} edge SN-88 tensile creep sample, 50 h



A-USAXS size distributions from SN-88 near the Yb L_{III} edge



Yb disilicate and tensile creep cavity size distributions from SN-88



Silicon Nitride Samples

Microstructure

- commercial grade of gas-pressure sintered silicon nitride (designated SN88 [1])
- β-Si_3N_4 grains
- major crystalline secondary phase after heat treatment is ytterbium disilicate, $Yb_2Si_2O_7$
- minor phases include residual $Yb_2Si_2N_2O_3$, $Y_2Si_3NO_{3.5}$, residual SiO_2 glass, and porosity.

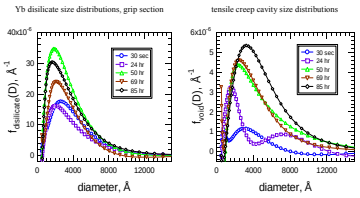
Sample Conditions

- Five tensile creep tests
- Different test times: 30 s – 85 h
- 1400° C, 150 MPa load
- Tests interrupted and cooled under load
- A-USAXS samples ground and hand-polished
- Sample from undeformed grip, 180 µm
- Sample from gage parallel to stress axis, 100 µm

[1] NGK Insulator Co., Ltd., Nagoya, Japan

[2] The use of commercial designations or company names is for identification only and does not indicate endorsement by the National Institute of Standards and Technology.

Evolution of size distributions with test time, 1400 C



Conclusions

- A-USAXS used to determine simultaneously Yb disilicate and creep cavity size distributions in SN-88
- Yb disilicate and creep cavities were of comparable size
- V_v of Yb disilicate 5-8 times greater than V_v of creep cavities
- V_v of creep cavities proportional to tensile strain, slope = 1
- Good agreement with density change data
- Confirmation that cavitation is the main creep mechanism
- A-USAXS obtained statistically-significant measurements of Yb-rich secondary phase pockets during creep in the presence of a creep cavity population of similar dimensions

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