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# DESTABILIZATION OF YTTRIA-STABILIZED ZIRCONIA INDUCED BY MOLTEN SODIUM VANADATE-SODIUM SULFATE MELTS*

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The extent of surface destabilization of $ZrO_2$ - 8 wt % $Y_2O_3$ ceramic disks was determined after exposure to molten salt mixtures of sodium sulfate containing up to 15 mole% sodium metavanadate ($NaVO_3$) at 1173 K. The ceramic surface was observed to transform from the cubic/tetragonal to monoclinic phase, concurrent with chemical changes in the molten salt layer in contact with the ceramic. Significant attack rates were observed in both pure sulfate and metavanadate-sulfate melts. The rate of attack was found to be quite sensitive to the mole fraction of vanadate in the molten salt solution and the partial pressure of sulfur trioxide ($1x10^6$ to $1x10^{-3}$ atm) in equilibrium with the salt melt. The observed parabolic rate of attack is interpreted to be caused by a reaction controlled by diffusion in the salt that penetrates into the porous layer formed by the destabilization. The parabolic rate constant in mixed sodium metavanadate - sodium sulfate melts was found to be proportional to the $SO_3$ partial pressure and the square of the metavanadate concentration. In-situ Raman spectroscopic measurements allowed simultaneous observations of the ceramic phases and salt chemistry during the attack process.

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Table I

Exposure Environment Composition

( percent )

| Initial Gas Composition | | Equilibrium Composition at 1173 K | | |
|---|---|---|---|---|
| $O_2$ | $SO_2$ | $O_2$ | $SO_2$ | $SO_3$ |
| 90 | 10 | 90 | 7.7 | 2.4 |
| 99 | 1 | 99 | .76 | .24 |
| 99.9 | 0.1 | 99.9 | $7.6x10^{-2}$ | $2.5x10^{-2}$ |
| 99.985 | 0.015 | 99.99 | $1.1x10^{-2}$ | $3.7x10^{-3}$ |
| 1 | 99 | .25 | 97. | .15 |

Table II

Parabolic Rate Constants

( $P_{SO_3} = 2.4 \times 10^{-3}$ )

| NaVO3 Concentration ( mole percent ) | Parabolic Rate Constant ( cm2/sec) |
|---|---|
| 0.0 | $1x10^{-11}$ |
| 0.2% | $1X10^{-11}$ |
| 1.0% | $1.7X10^{-10}$ |
| 2.0% | $5.4x10^{-10}$ |
| 3.9% | $1.5x10^{-9}$ |

## *RAMAN EFFECT*

$$\omega_I - \omega_S = \omega_{VIB}$$

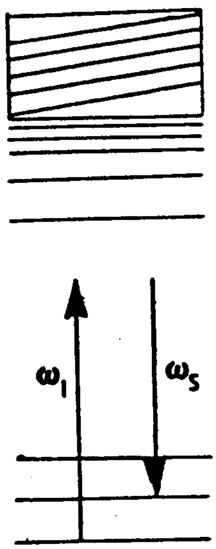



Figure 1.

RAMAN BACKSCATTERING CONFIGURATION

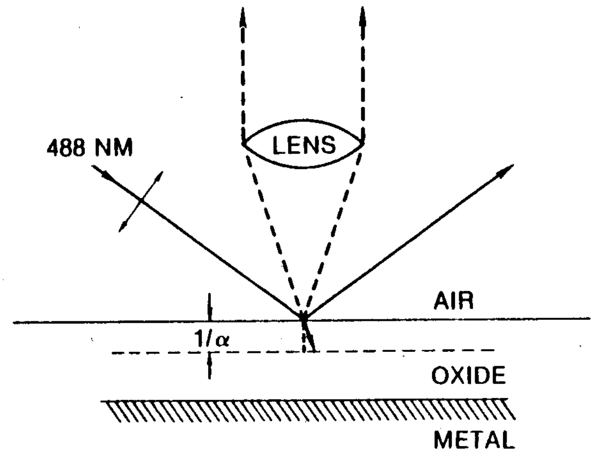



Figure 2.

RAMAN ADVANTAGES

1. NON-PERTURBING
2. <u>IN</u> <u>SITU</u>
3. QUANTITATIVE CHEMICAL COMPOUND IDENTIFICATION
4. SENSITIVE TO LATTICE SYMMETRY
5. LATERAL RESOLUTION - 1 $\mu m$
6. DEPTH RESOLUTION - (100 Å - 100 $\mu m$)
7. GAS ENVIRONMENT CHARACTERIZATION
8. SAMPLE/GAS TEMPERATURE
9. TEMPORAL RESOLUTION (ms - hs)

Figure 3.

$ZrO_2 - Y_2O_3$

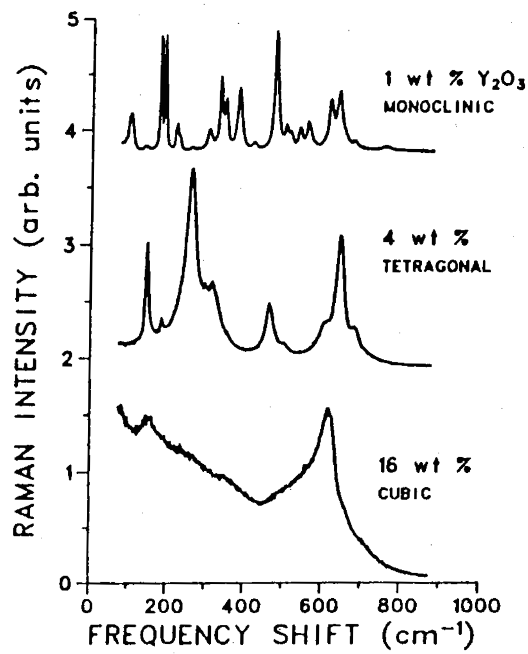



Figure 4.

## Experimental Proceedure

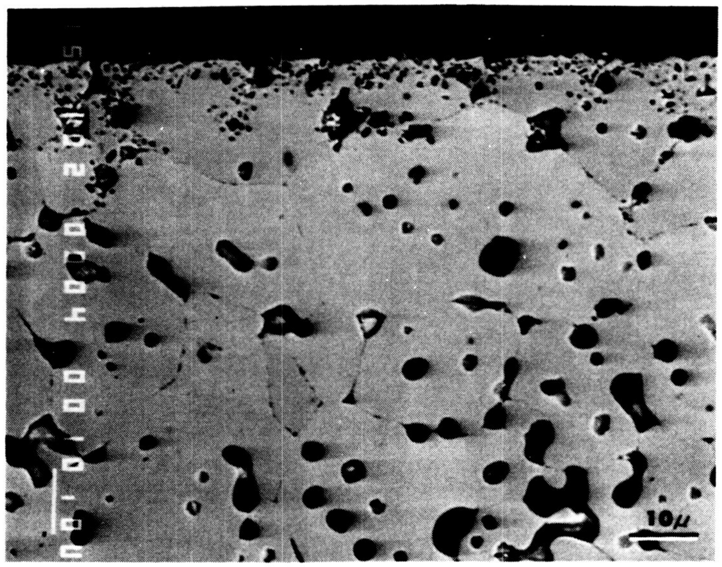
- Stabilized zirconia ceramics immersed in sulfate-vanadate melts contained in platinum crucibles.
- Temperature, sulfur dioxide and sulfur trioxide content varied.
- Post-exposure analysis by electron microscopy, electron microprobe and Raman spectroscopy.

Figure 5.

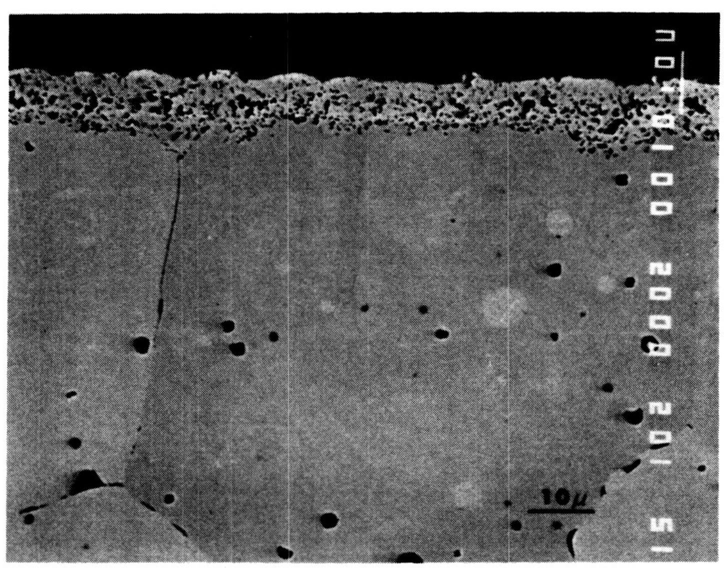
## $ZrO_2$ – 8 wt% $Y_2O_3$

**Exposure:** 900°C

Pure $Na_2V_2O_6$




10 min.




1 hr.

Figure 6.

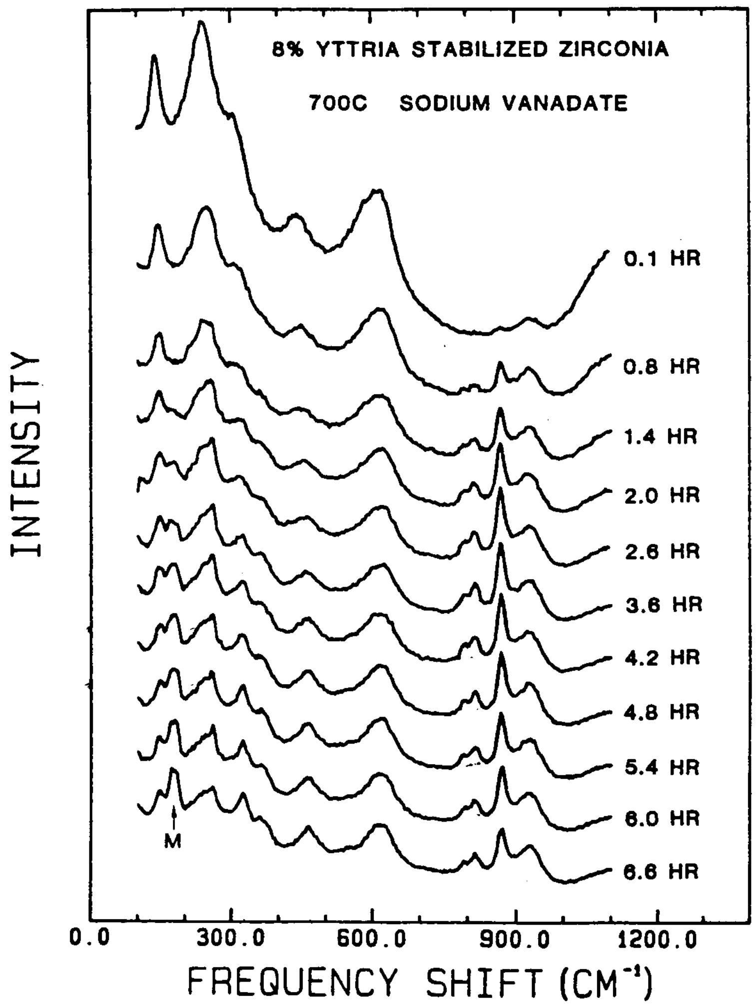



Figure 7.

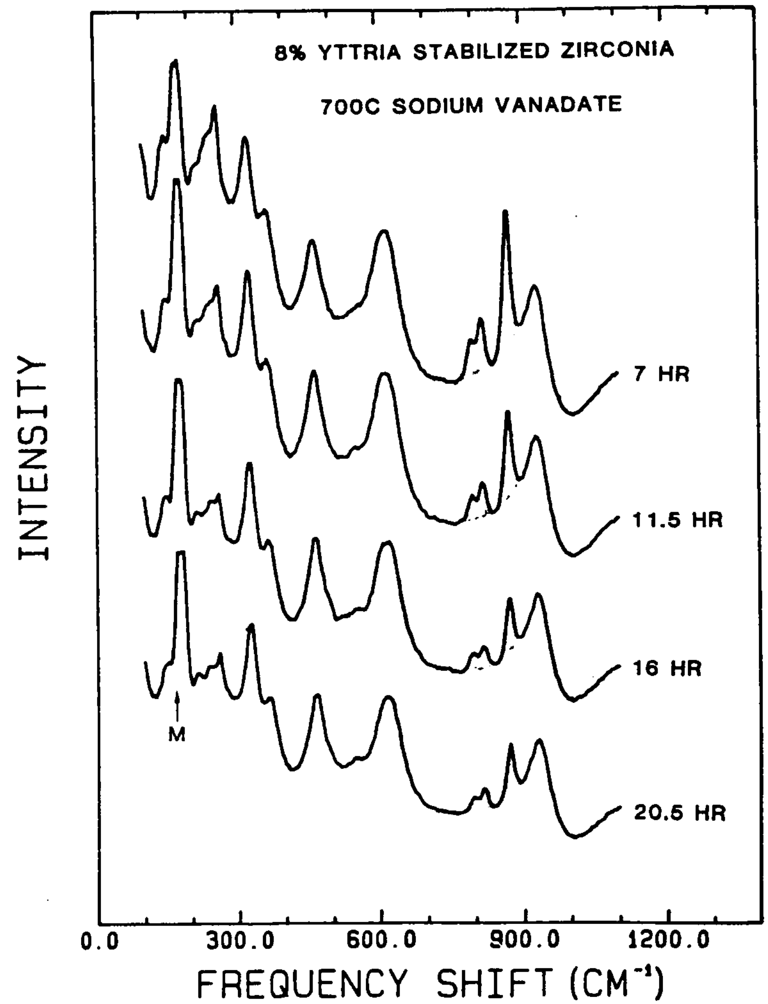



Figure 8.

$ZrO_2$ - 8wt% $Y_2O_3$
$NaVO_3$ 24hr 700°C

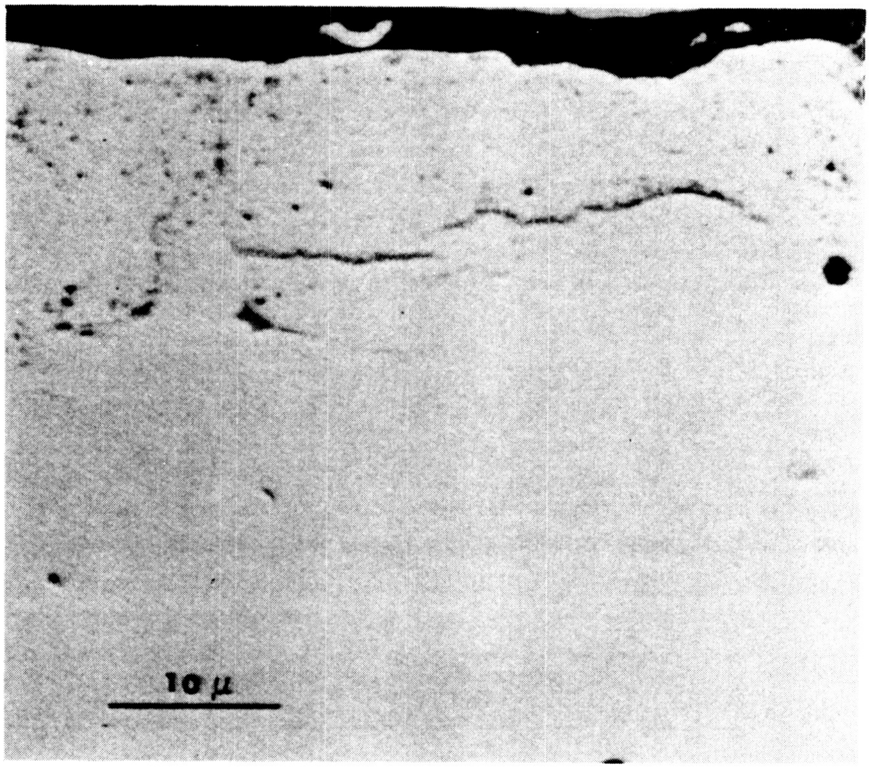



Figure 9.

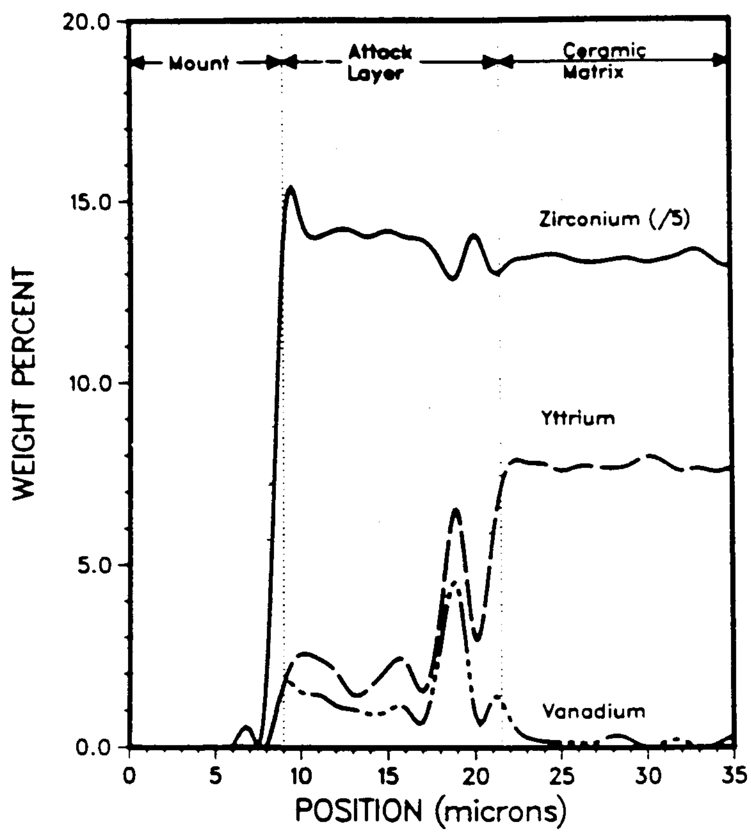



Figure 10.

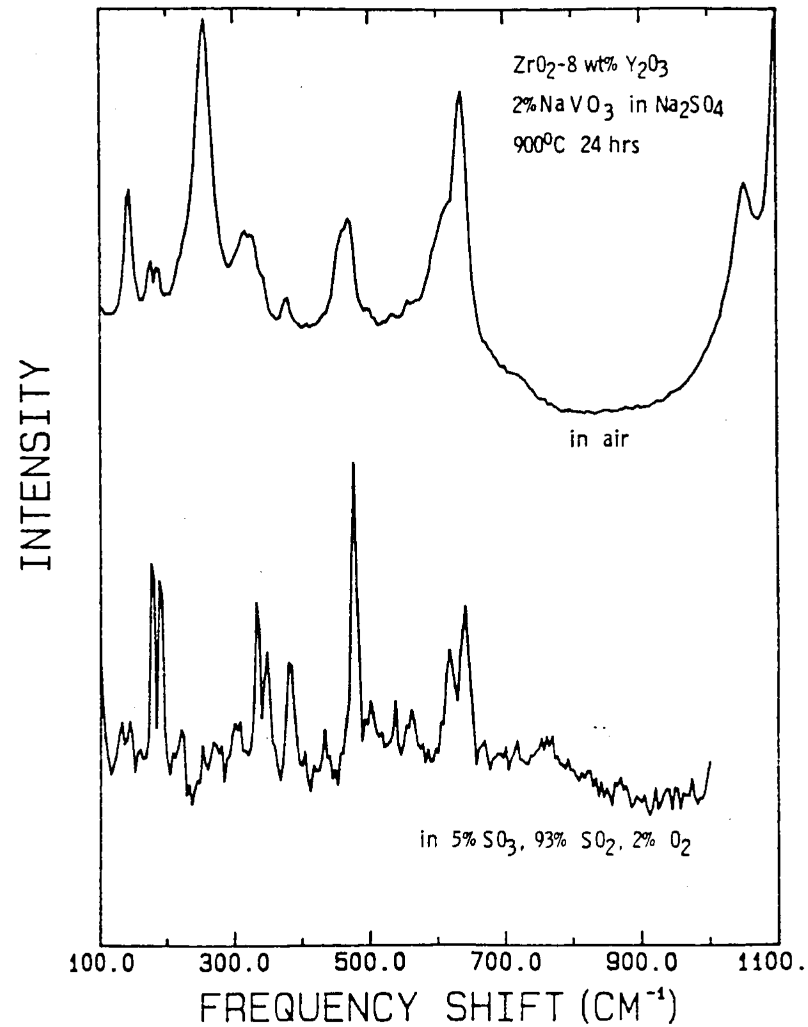
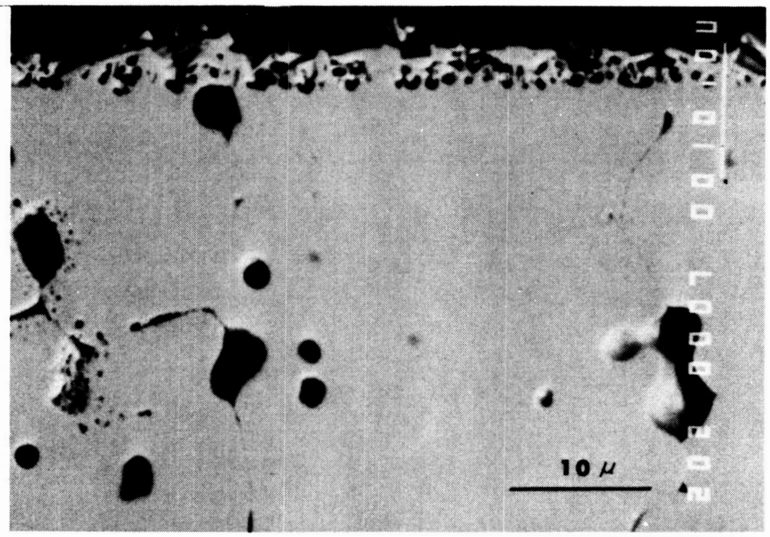



Figure 11.

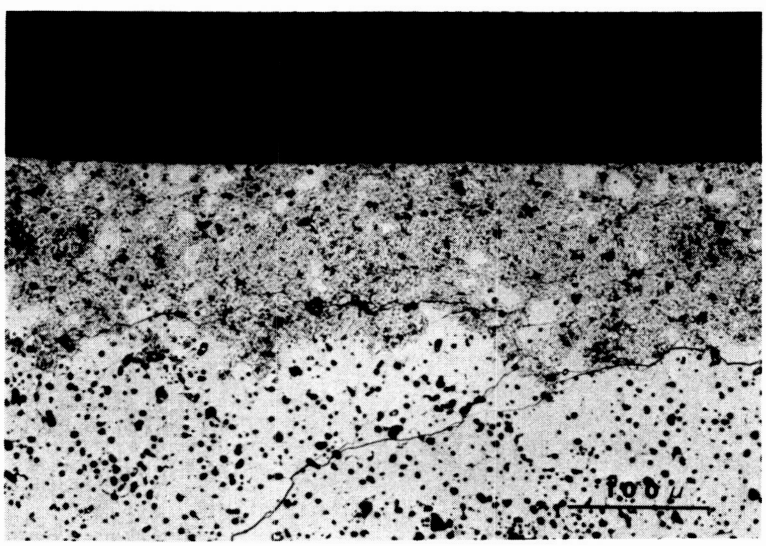
# $ZrO_2$ – 8 wt% $Y_2O_3$

Exposure: 900°C 24 hr.

2 mol% $Na_2V_2O_6$ in $Na_2SO_4$




Exposed in air




Exposed to 93% $SO_2$ 5% $SO_3$ 2% $O_2$

Figure 12.

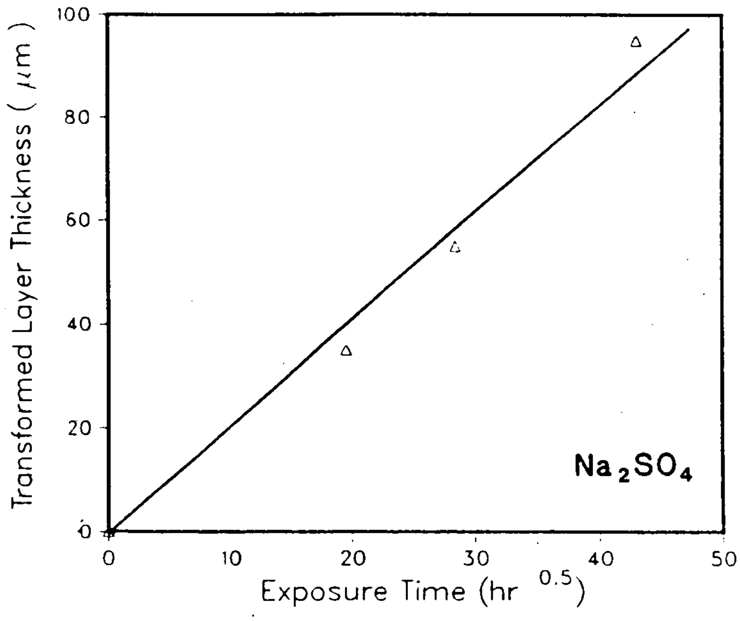



Figure 13.

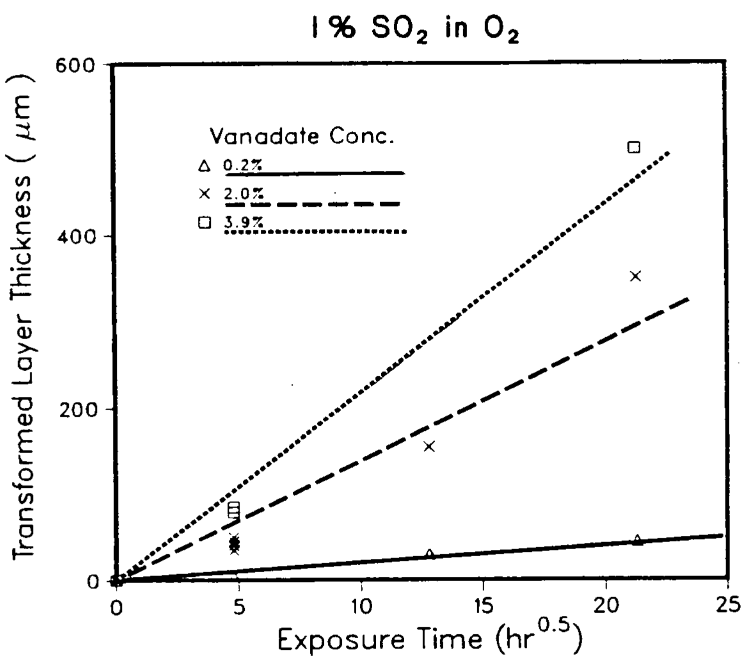



Figure 14.

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OF POOR QUALITY

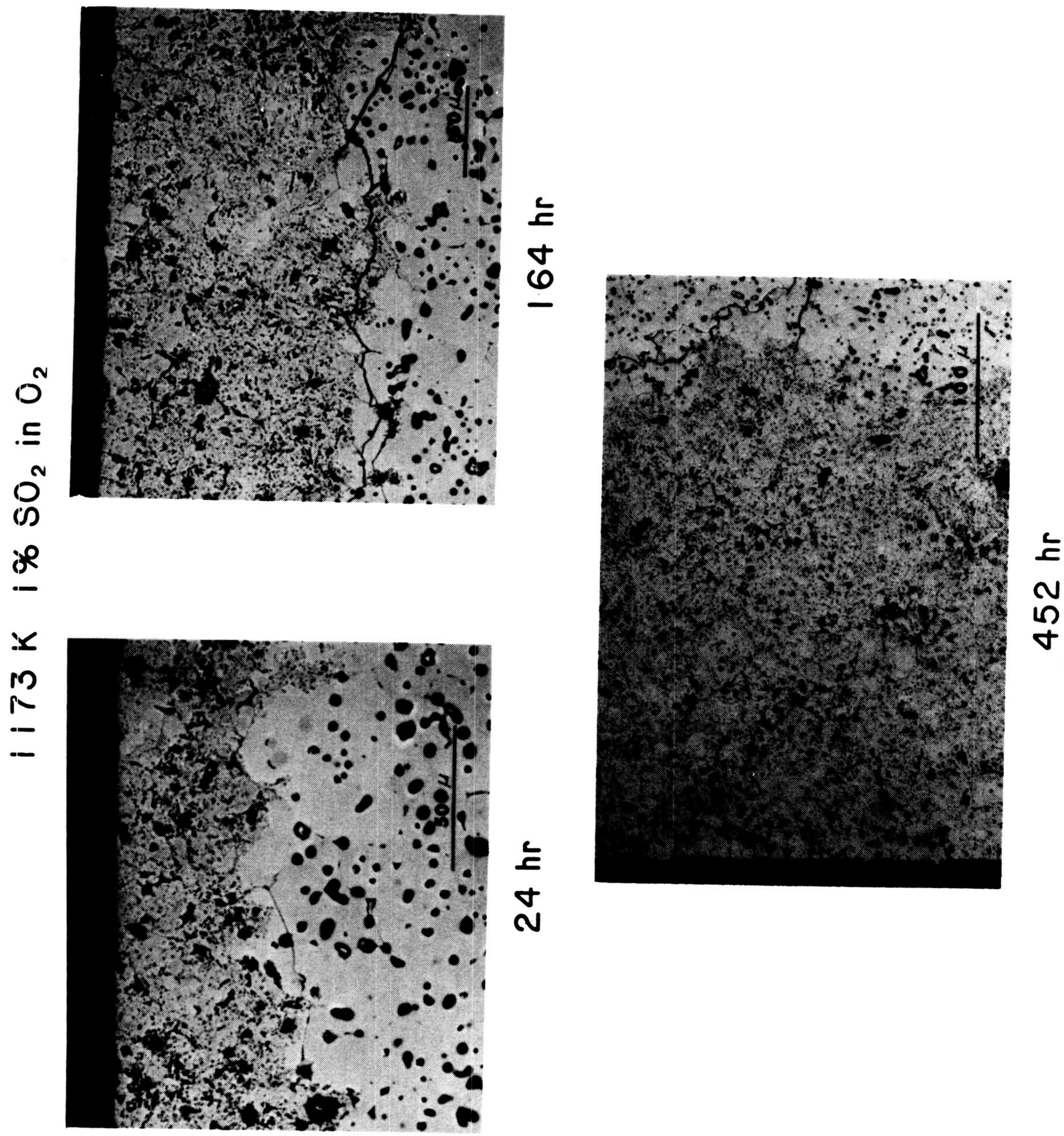



Figure 15.

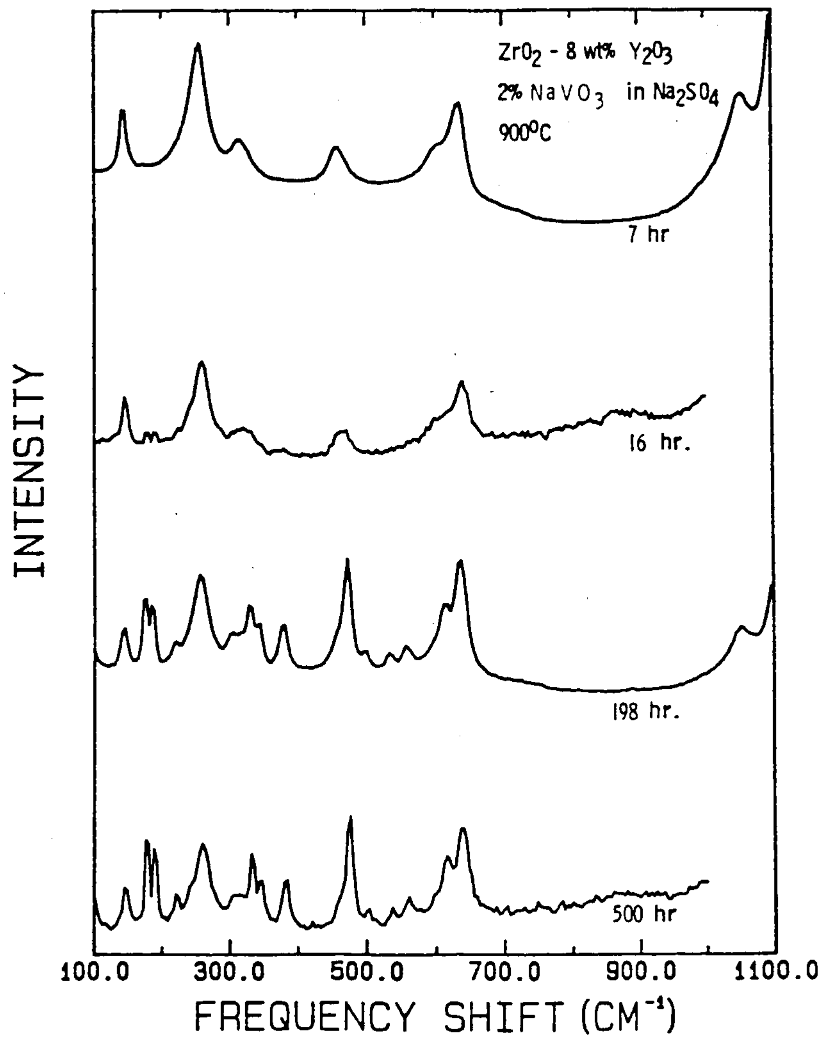



Figure 16.

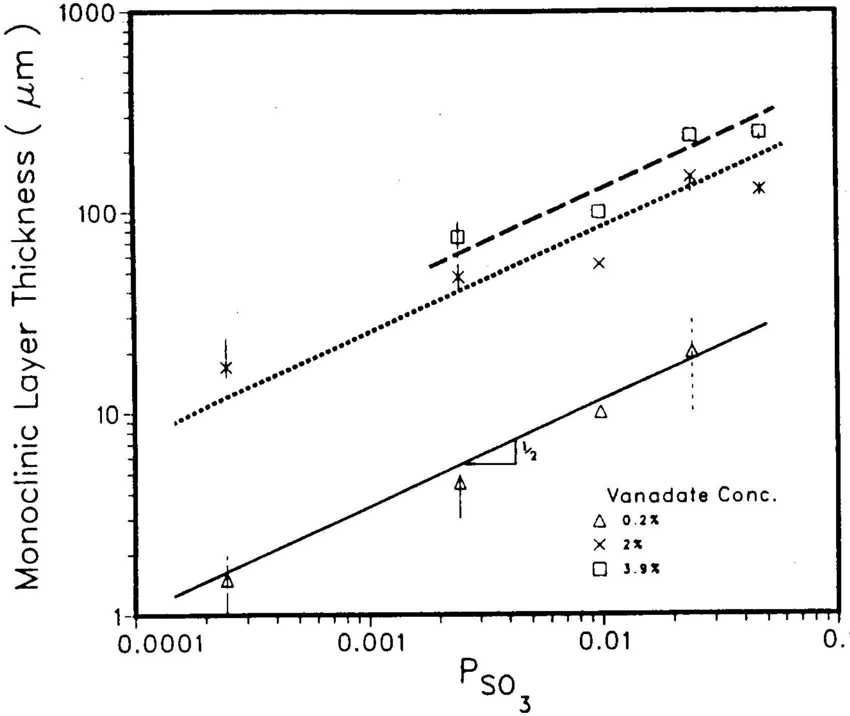



Figure 17.

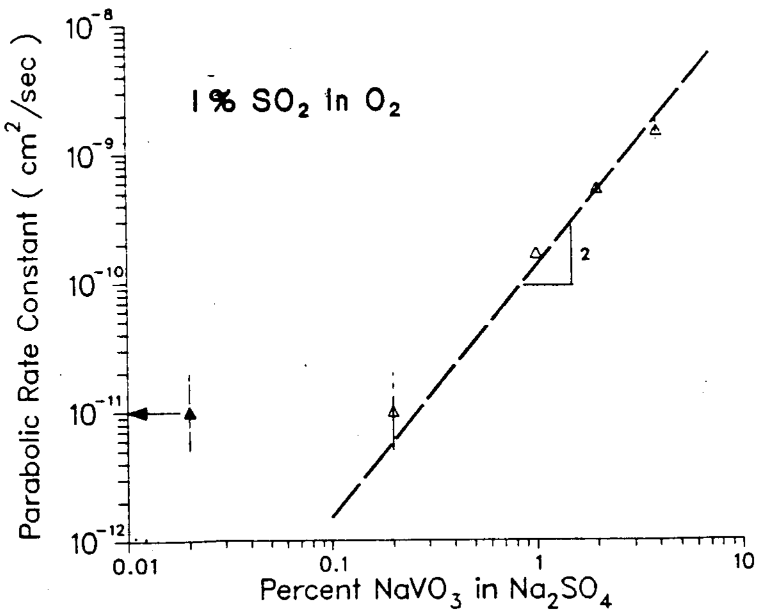



Figure 18.

## YTTRIUM LEACHING REACTIONS

– in sulfate melts

$$Y_2O_3 + 3\ SO_3 \rightleftharpoons 2\ Y^{+3} + 3\ SO_4^{-2}$$

– in sulfate–vanadate melts

$$Y_2O_3 + V_2O_5 \rightleftharpoons 2\ Y^{+3} + 2\ VO_4^{-3}$$

Figure 19.

$$SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$$

$$Na_2SO_4 \rightleftharpoons Na_2O + SO_3$$

$$a_{Na_2O} = \frac{K_2}{p_{SO_3}}\ a_{Na_2SO_4}$$

$$2\ NaVO_3 \rightleftharpoons Na_2O + V_2O_5$$

$$a_{V_2O_5} = \frac{K_3\ a_{NaVO_3}^2}{a_{Na_2O}} = \frac{K_3\ p_{SO_3}\ a_{NaVO_3}^2}{K_2\ \ a_{Na_2SO_4}}$$

Figure 20.

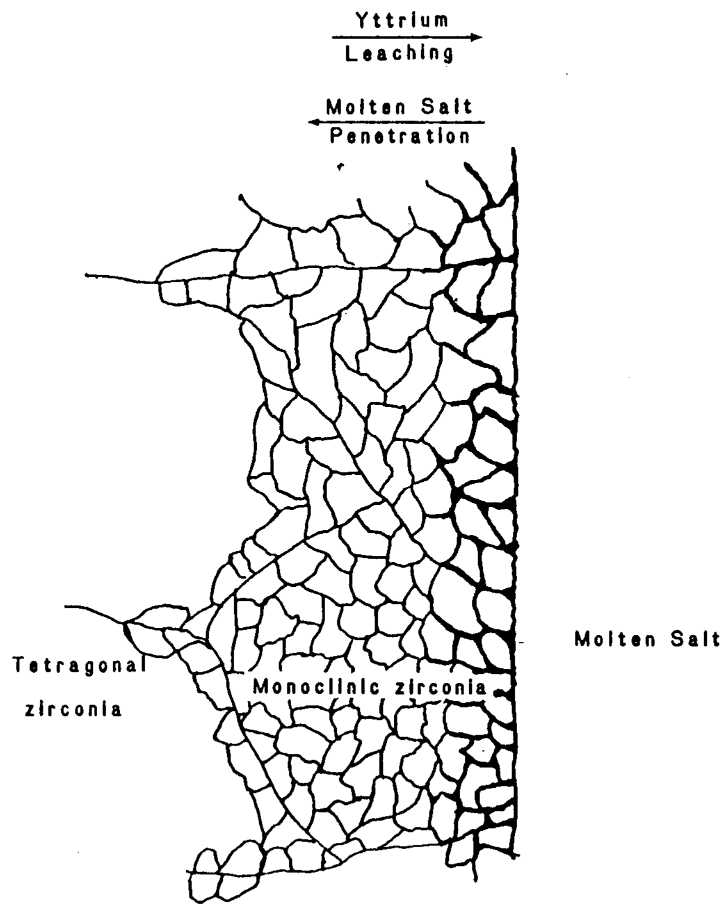
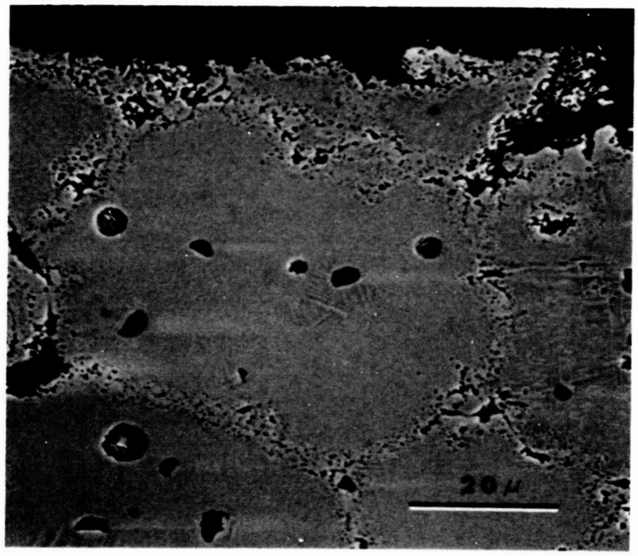


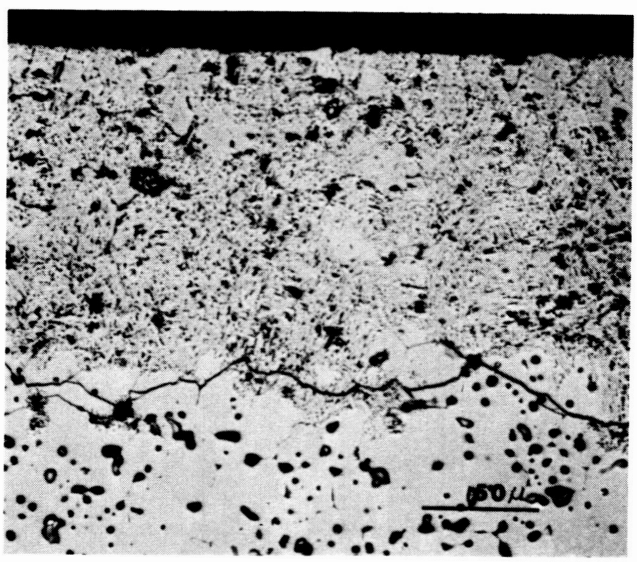

Figure 21.

# 1173 K 1% $SO_2$ in $O_2$




$ZrO_2$ – 1.5 wt% MgO

96 hr




$ZrO_2$ – 8 wt% $Y_2O_3$

164 hr

Figure 22.

## Summary

- Attack of zirconia ceramics is sensitive to sodium metavanadate concentration, and thus to vanadium impurity level in fuel.

- The attack is also sensitive to sulfur dioxide content of the environment.

- The attack follows parabolic kinetics and is proportional to the square root of the sulfur trioxide partial pressure.

Figure 23.