

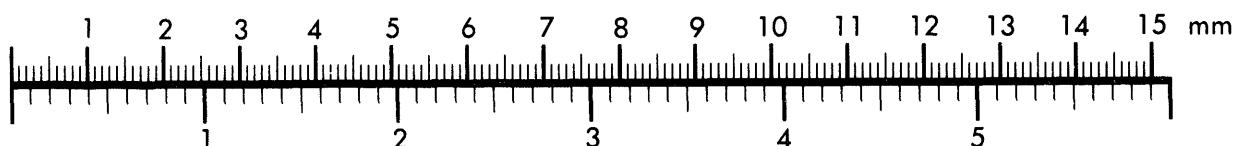


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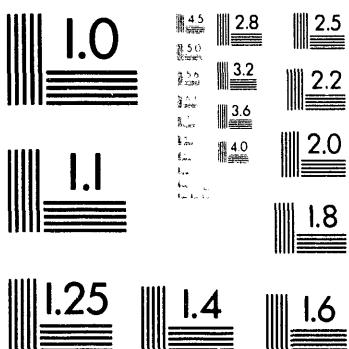
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HIGH TEMPERATURE ALKALI CORROSION OF CERAMICS
IN COAL GAS

DE-FG22-91PC 91309

Quarterly Progress Report #11
for the Period
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Objective/Scope

High temperature alkali corrosion has been known to cause premature failure of ceramic components used in advanced high temperature coal combustion systems such as coal gasification and clean-up, coal fired gas turbines, and high efficiency heat engines. The objective of this research is to systematically evaluate the alkali corrosion resistance of the most commonly used structural ceramics including silicon carbide, silicon nitride, cordierite, mullite, alumina, aluminum titanate, zirconia, and fireclay glass. The study consists of identification of the alkali reaction products (phase equilibria) and the kinetics of the alkali reactions.

Technical Progress

Mullite Alkali Corrosion Kinetics

The alkali corrosion kinetics of mullite (Superior Technical Ceramics, Inc.) were investigated in a constant partial pressure of sodium nitrate. As previously described, the constant alkali vapor pressure was generated by flowing compressed air (filtered to remove carbon dioxide and moisture) at 200 ml/min over the sodium nitrate salt maintained at 715°C and monitoring the weight loss of the salt. After passing through the salt chamber, the gases flowed into the reaction chamber where the samples were

held at the appropriate temperature. The concentration of sodium nitrate was calculated to be approximately 0.90 vol%. The mullite pellets (approximately 3x3x6 mm) were placed vertically in an alumina holder containing alumina powders to support the specimens and were isothermally heated at the appropriate temperatures from 2 h to 15 h. The thickness of the mullite samples before and after the alkali corrosion was measured using a micrometer (Starrett model 230M). The reaction layer thickness was calculated as the difference between the thickness after and before corrosion. The reaction products were identified using x-ray diffraction (XRD). The microstructure of the corroded specimen was examined and compared to that of the as-received specimen using a scanning electron microscope.

The reaction thickness of the mullite in the alkali-containing atmosphere versus reaction time is shown in Figure 1. The reaction layer thickness appears to be linearly related to the reaction time. The linear reaction rate constants are 6, 10, 25 and 39 $\mu\text{m}/\text{h}$ at 950°C, 1000°C, 1050°C and 1100°C respectively. X-ray diffraction analysis of the as-received material showed only mullite and a trace of corundum were present. No cristobalite was detected. Density measurements (using archimedes method) gave a true density of 3.004 and a bulk density of 2.998 g/cc for the as-received material. Elemental analysis using EDAX (energy dispersive analysis of x-rays) measurements of the samples (which were cut on a diamond saw) before corrosion show only aluminum and silicon as the major constituents with trace iron, copper and potassium.

EDAX measurements after corrosion at 1000°C for 8 h show only aluminum, silicon

and sodium. X-ray diffraction analysis of the mullite specimens after reaction in the alkali-containing atmosphere revealed the presence of sodium aluminate and carnegieite. The peaks in the diffraction pattern shift slightly as a function of reaction time at 1000°C suggesting that there might be some solid solution of the sodium aluminate and the carnegieite phases.

Figure 2 shows the SEM micrographs of the as-received mullite and the specimen corroded at 1000°C for 8 h. The reaction layer exhibits a large number of microcracks as can be seen in Figure 2b. It is not certain whether these cracks form during the reaction process as a result of the differences in volumes of the substrate and the corrosion products or whether they form during the cooling period due to differences in the thermal expansions of the substrate and the corrosion layer.

Zirconia Alkali Corrosion Kinetics

The alkali corrosion kinetics of zirconia (TTZ, Coors) at 950°C is shown in Figure 3. The SEM micrographs of the as-received zirconia fracture surface and after reaction at 950°C is shown in Figure 4. As seen in this figure, the transformation toughened zirconia is very dense with only a few isolated pores occurring within the grains. The alkali reaction product after a 950°C for 15 h exposure, however, is very porous in comparison to the as-received material.

Cordierite Alkali Corrosion Kinetics

The alkali corrosion kinetics of cordierite (Coors) were also studied at 950°C. The thickness of the alkali reaction layer versus time is shown in Figure 5. The SEM micrographs of the as-received cordierite fracture surface and the surface after reaction at 950°C is shown in Figure 6. The as-received material appears very dense, as shown in Figure 6a. The alkali reaction layer that forms on the surface of the cordierite pellet after alkali exposure at 950°C for 15 h is very porous as shown in Figure 6b.

Aluminum Titanate Alkali Corrosion Kinetics

The alkali corrosion kinetics of aluminum titanate at 950°C were also investigated. The aluminum titanate pellet undergoes a severe reaction at 950°C with the alkalis. Aluminum titanate (without stabilizing agents) is not stable below about 1250°C where it decomposes into alumina and titania. It may be that the severity of the alkali reaction is due to the decomposition of the aluminum titanate and subsequent reaction of the alumina and titania with the alkalis. More experimentation will be performed to try to determine if this is indeed the case. The SEM micrographs of the as-received aluminum titanate fracture surface and after alkali reaction at 950°C is shown in Figure 7. The alkali reaction kinetics at the higher temperatures for zirconia, cordierite and aluminum titanate will be completed for the next reporting period.

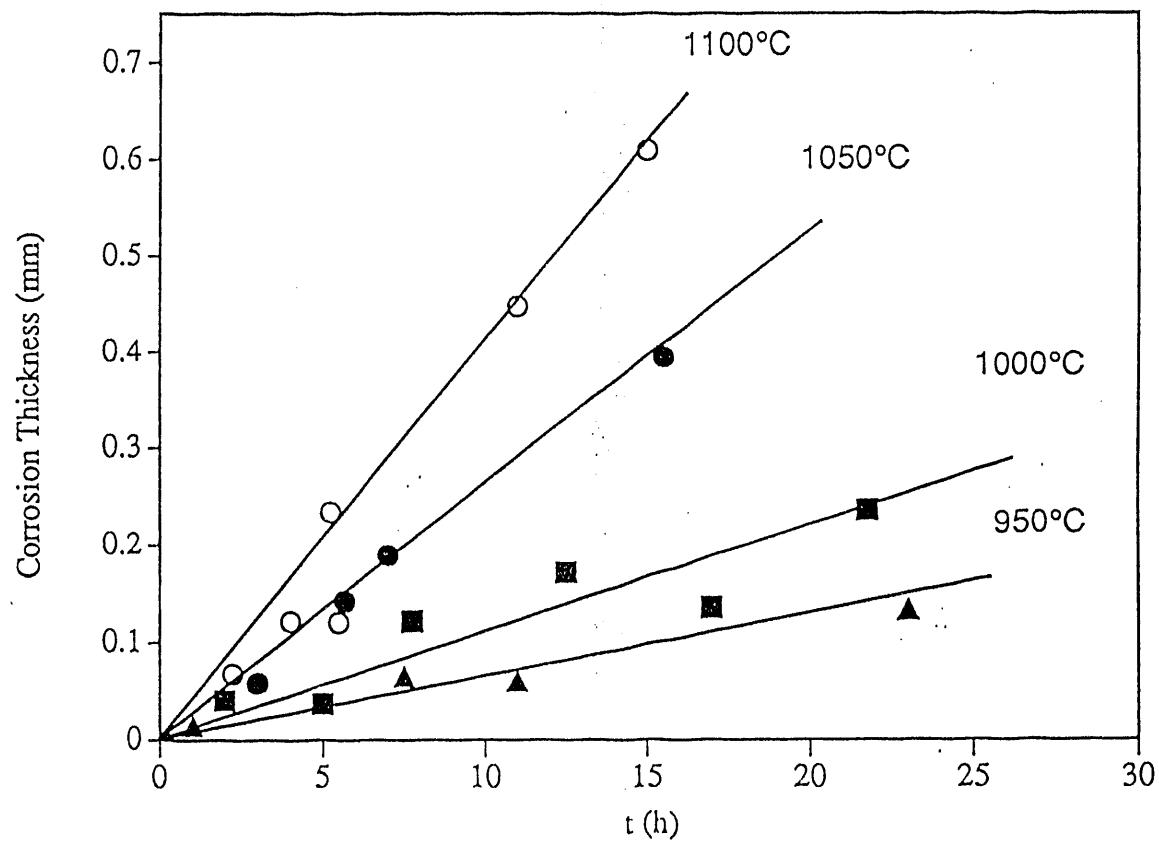


Figure 1. Mullite reaction layer thickness versus time

a.)



b.)



Figure 2. SEM micrograph of (a) as-received mullite and (b) after 8 h at 1000°C

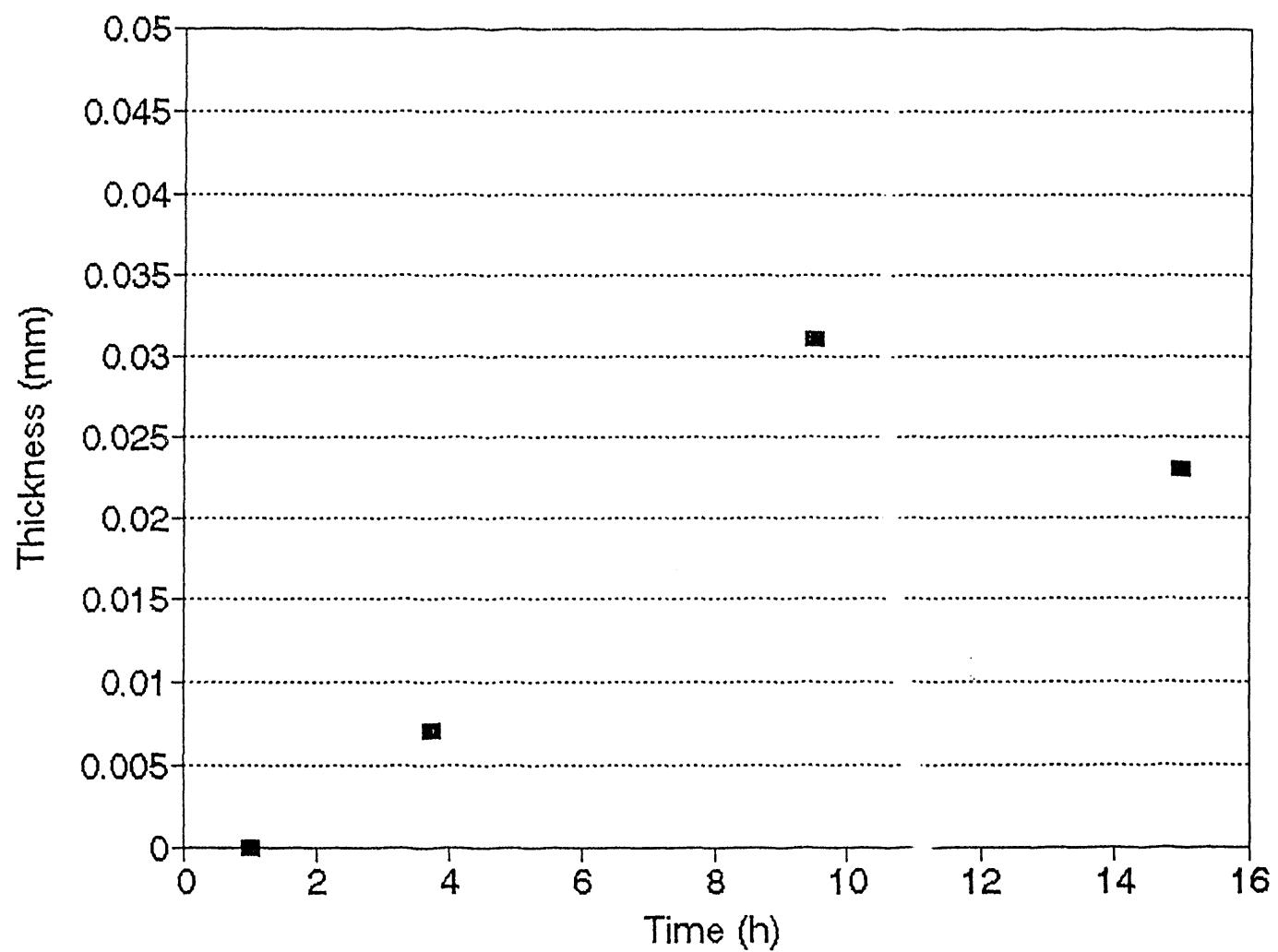
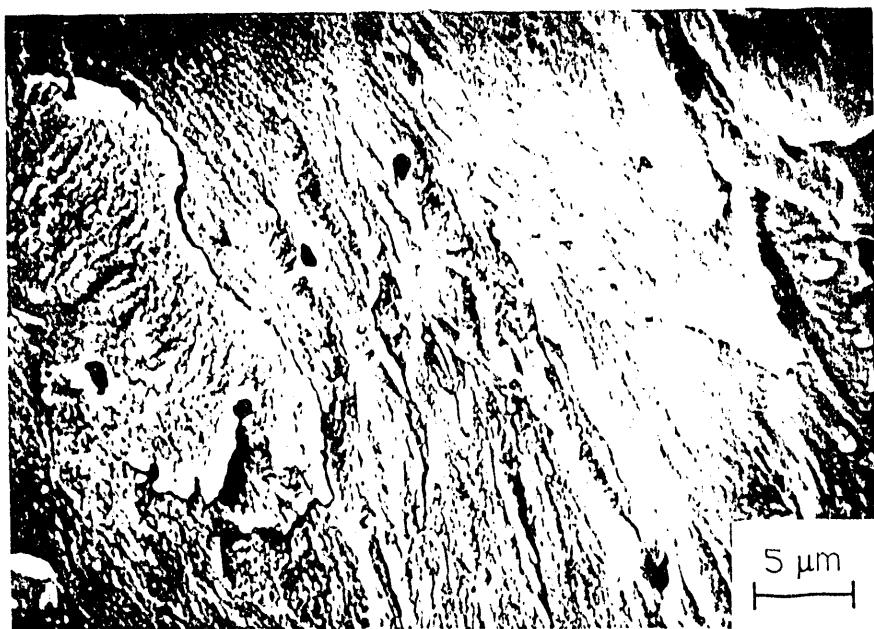


Figure 3. Zirconia reaction layer thickness versus time

a.)



b.)

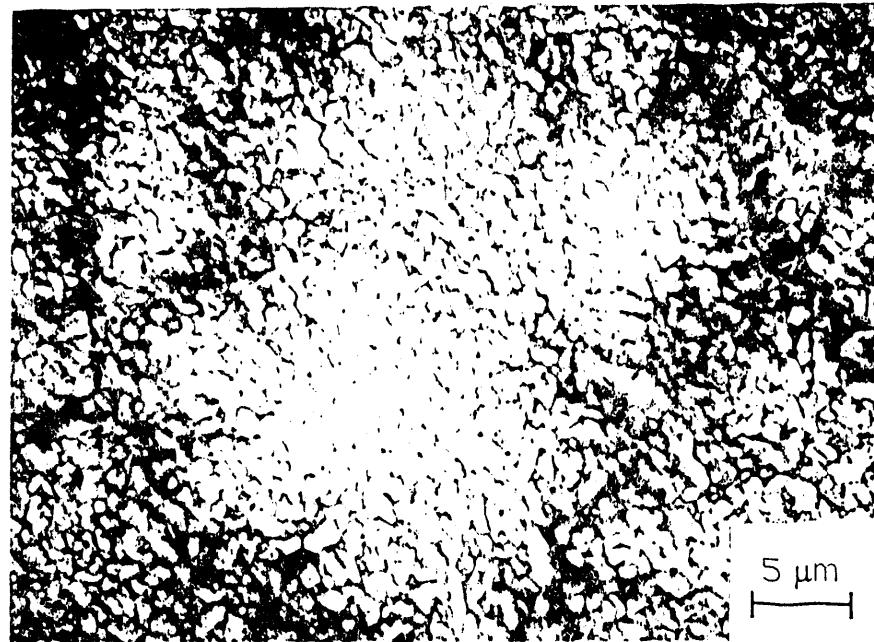


Figure 4. SEM micrograph of (a) fracture surface of as-received ZrO₂ and (b) ZrO₂ after 15 h at 950°C, glass etched away

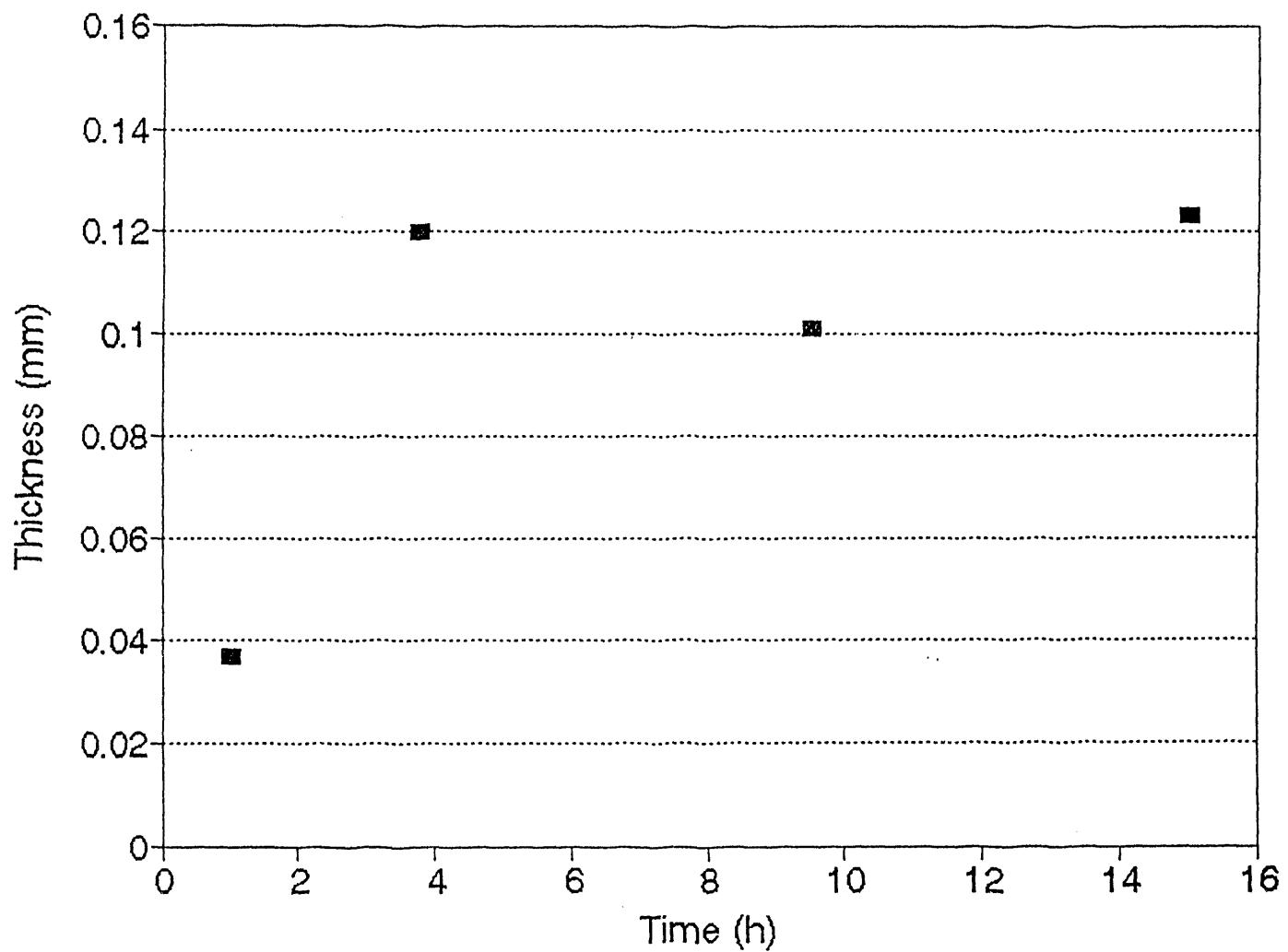
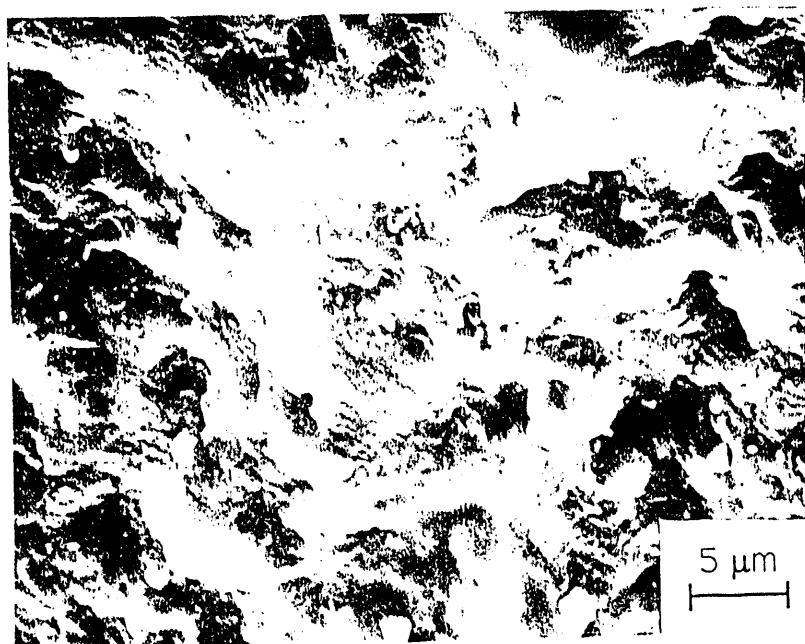


Figure 5. Alumina titanate reaction layer thickness versus time

a.)



b.)

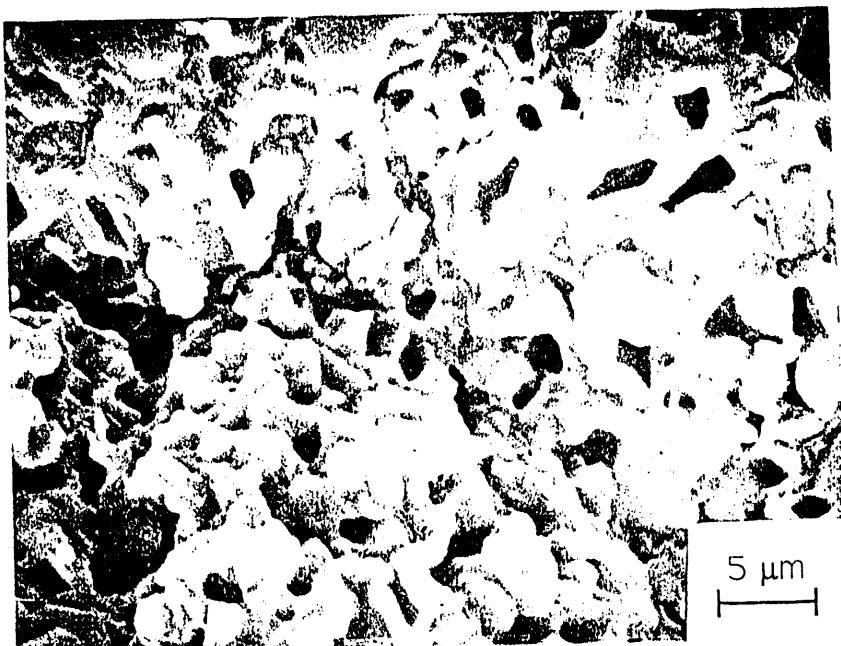
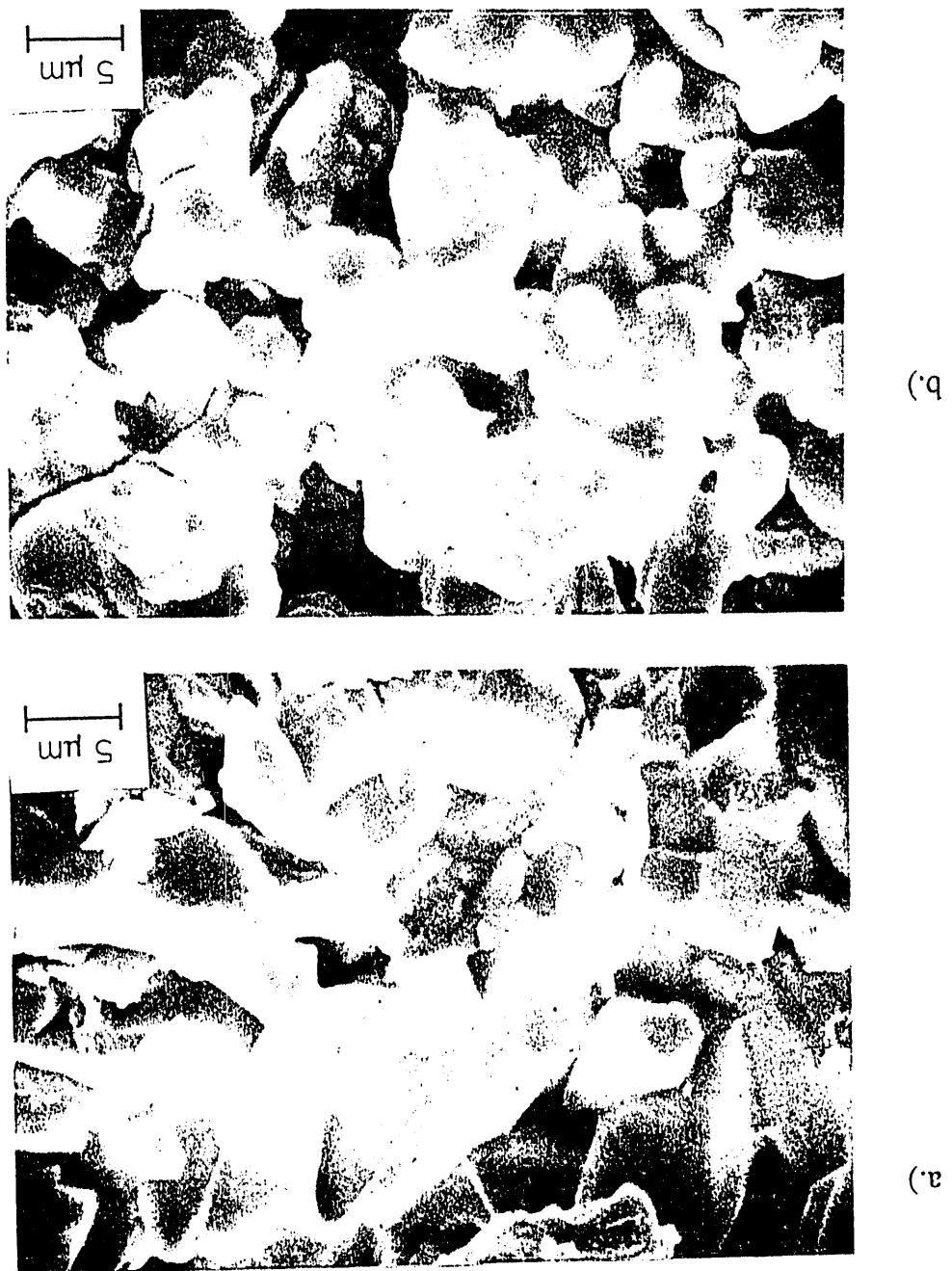


Figure 6. SEM micrograph of (a) fracture surface of as-received cordierite and (b) cordierite after 15 h at 950°C, glass etched away

Figure 7. SEM micrograph of (a) fracture surface of as-received aluminum titanate
and (b) aluminum titanate after 3 h at 950°C, glass etched away



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