Oxidation Resistance of Si_3N_4 Ceramics Modified with Boron and Transition Metal Compounds

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Workshop: "New Developments in Silicon Nitride and Environmental Barrier Coatings for Microturbine and Industrial Gas Turbine Hot-Section Components"

November 6-7, 2002
Nashville, TN

Acknowlegments

- Dr. Steven Fishman for funding of the project.
- Dr. Boris Varshal for valuable discussions of glass structural aspects.
- Jessica Walker (On rotational assignment) and Kathryn Hinton (SEAP student) for help in experimental work

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Introduction

• Oxidation behavior of non-oxide ceramics highly depends on the properties of the oxidation product.

• NSWC Ceramics discovered a correlation between oxidation resistance of transition metal borides and the presence and extent of phase separation (immiscibility) in the surface protective glass formed during exposure to oxidizing atmosphere.

• Oxidation resistance of ZrB_2, TiB_2, TaB_2, NbB_2, and CrB_2 ceramics was significantly improved by their modification with SiC and in succession with each other as a result of the formation of phase-separated borosilicate glass containing transition metal oxides.

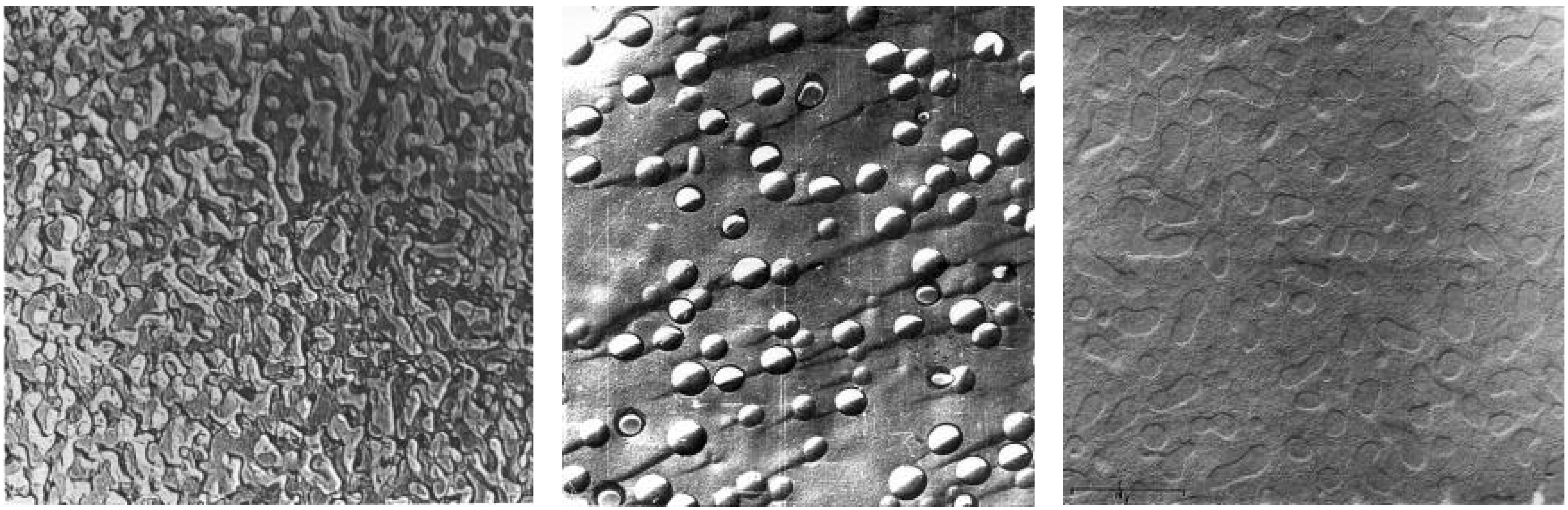
• Borate and silicate glasses containing Group IV-VI transition metal oxides show strong tendency to immiscibility. The systems exhibiting immiscibility have steeply rising liquidus temperatures and increased viscosity in the two-liquid composition range.

• The tendency to immiscibility is proportional to cation field strength, $\mathbf{z/r^2}$, where **z**=valence of element and **r**=ionic radius

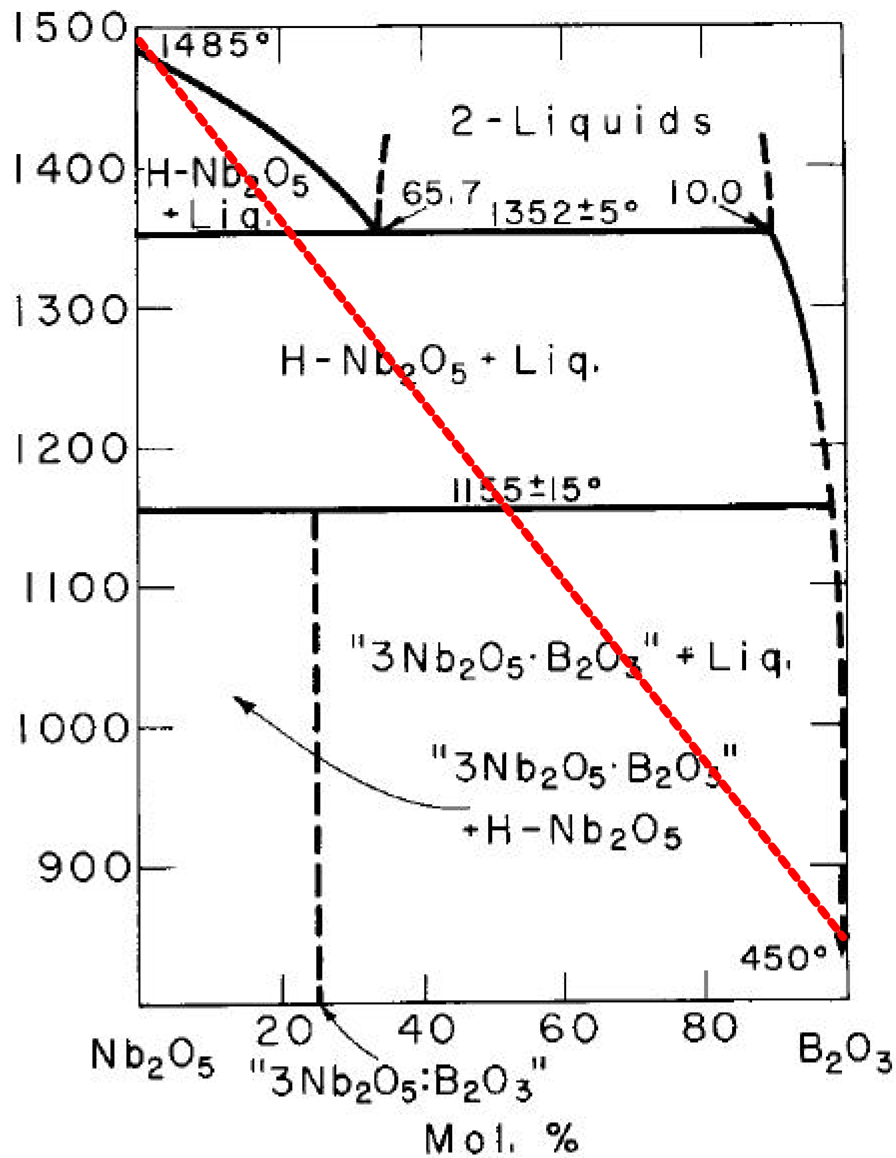
• The concept of using surface glass immiscibility to improve oxidation resistance was applied to Si_3N_4, ZrB_2/Si_3N_4, and Ti_3SiC_2 ceramics.

Typical Patterns of Glass Immiscibility

(SEM Images)



Phase Diagram of the System $Nb_2O_5 - B_2O_3$

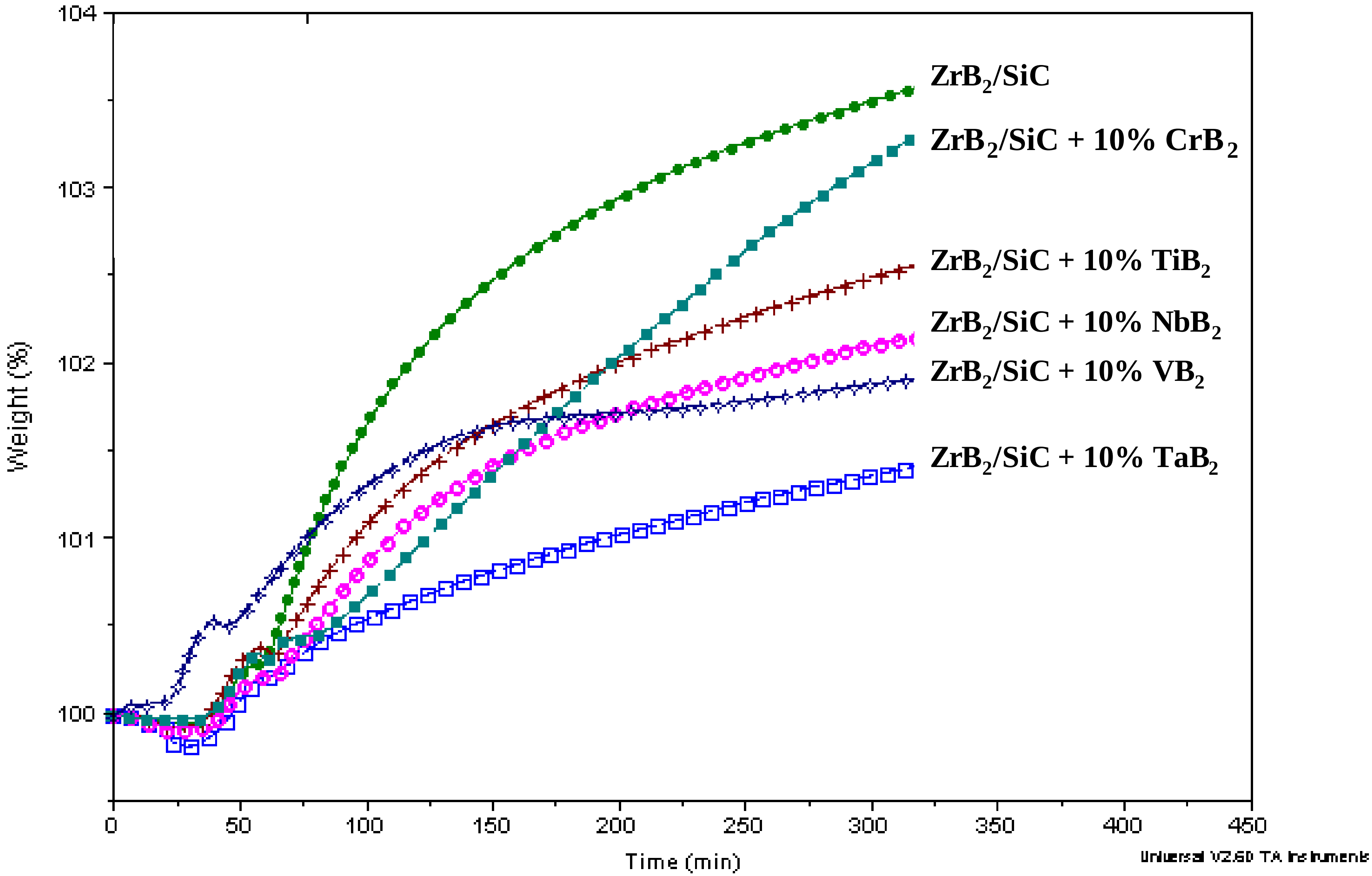


Cation Field Strength

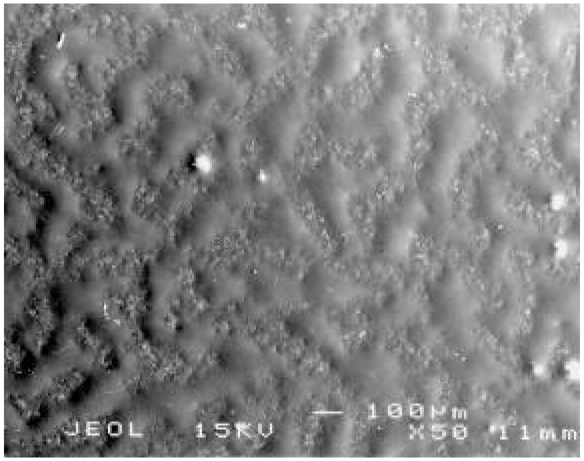
Cation/Valence (Z)	Radius r, (nm)*	Cation Field Strength Z/r^2, (nm^{-2})
Zr^{+4}	0.072	772
Cr^{+3}	0.0615	793
Cr^{+4}	0.055	1,322
Nb^{+4}	0.068	865
Nb^{+5}	0.064	1,220
Ta^{+5}	0.064	1,220
Ti^{+3}	0.067	668
Ti^{+4}	0.0605	1,093
V^{+3}	0.064	732
V^{+4}	0.058	1,189
V^{+5}	0.054	1,715

* The values of ionic radii are taken from R.D. Shannon, Acta Cryst. A32, 761-767,(1976)

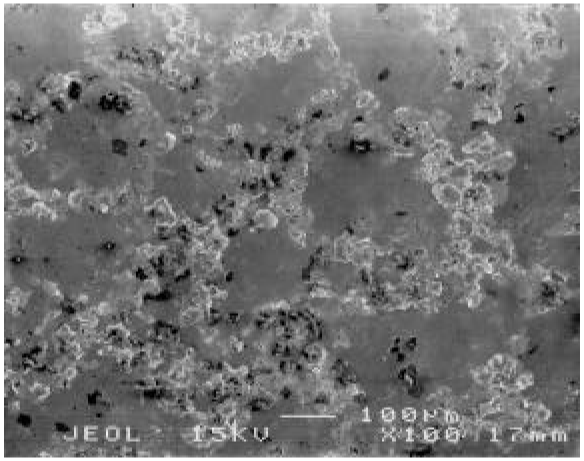
TGA Oxidation of Modified ZrB_2/SiC Ceramics at 1300°C



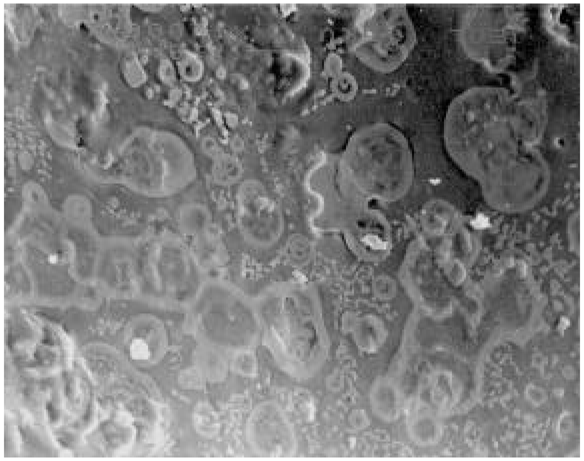
SEM Micrograph of the Surface of Oxidized ZrB_2/SiC Ceramics Modified with TaB_2, CrB_2, NbB_2, and VB_2



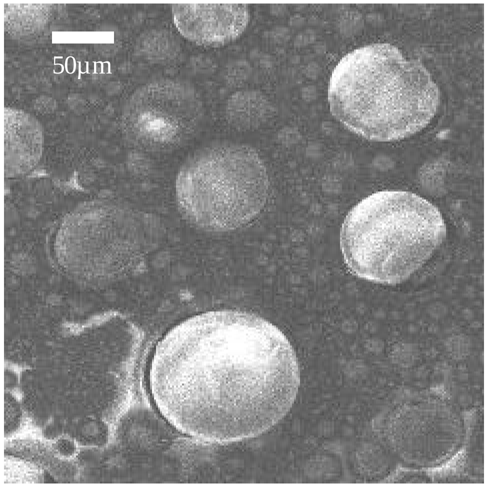
ZrB_2/SiC/TaB_2



ZrB_2/SiC/NbB_2



ZrB_2/SiC/CrB_2



ZrB_2/SiC/VB_2

Objective

Improve the oxidation resistance of Si_3N_4 ceramics by modification of the bulk composition and, consequently, the composition of the in-situ formed protecting surface oxide (glass) layer, applying the immiscibility-based control of oxidation behavior.

Experimental Procedure

- **Sample Composition:**

  - **Baseline material** - Si_3N_4 + 2% Al_2O_3 + 5% Y_2O_3 (wt.%)

  - Baseline Si_3N_4 ceramics were modified with 10 mole % CrB_2, ZrB_2, TaB_2, 5 to 10 mole % Cr_2O_3, ZrO_2, and Ta_2O_5, and 20 mole % BN.

- **Samples were hot-pressed at 1825ºC and 20MPa in He for 1 hour**

- **Oxidation Conditions:**

  - Furnace heating in air at 1200 - 1600EC for 2 hours

- **Characterization:**

  - Phase composition of the bulk and oxidized ceramics (XRD)
  - SEM of the bulk and oxidized surface of the ceramics

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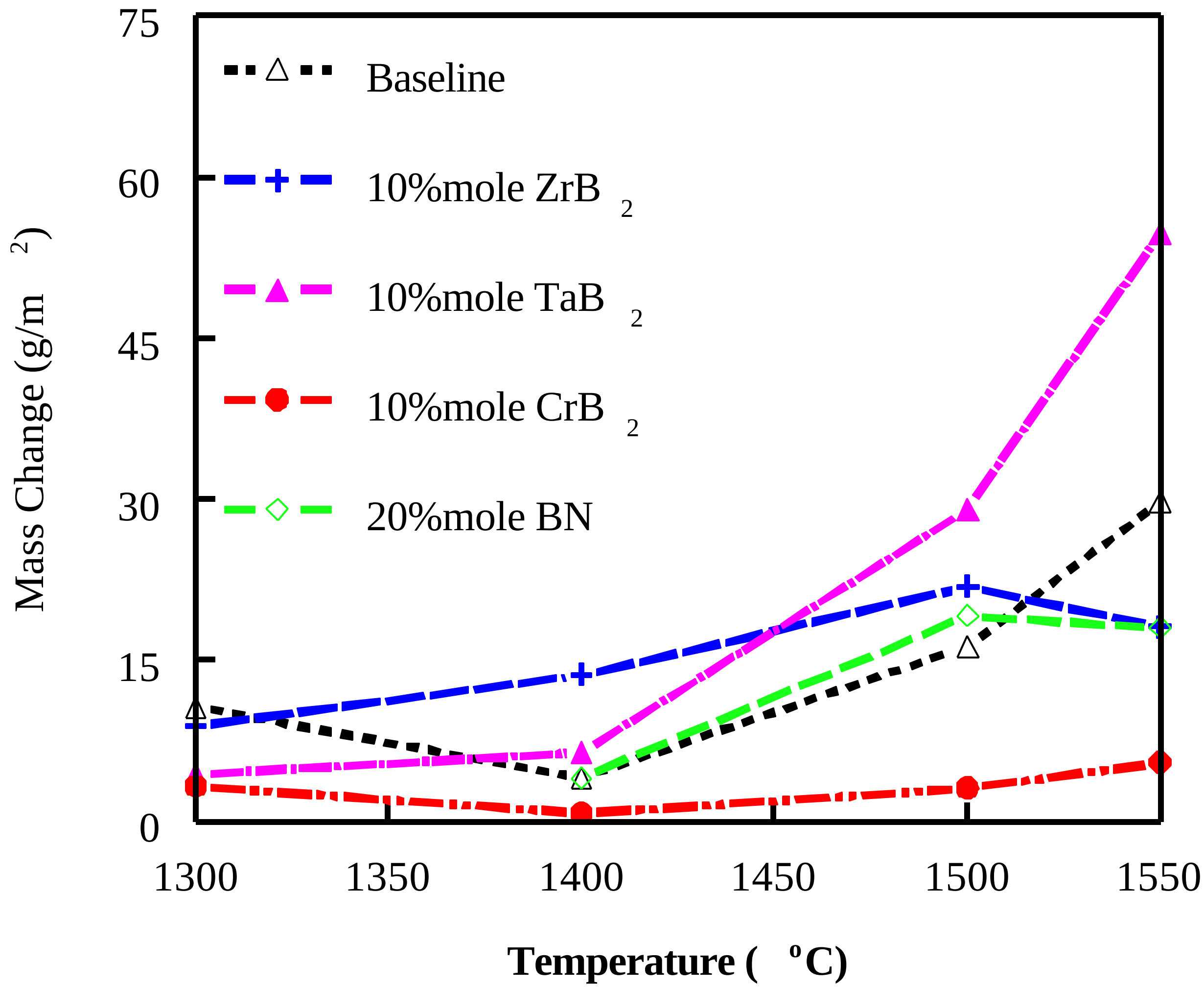
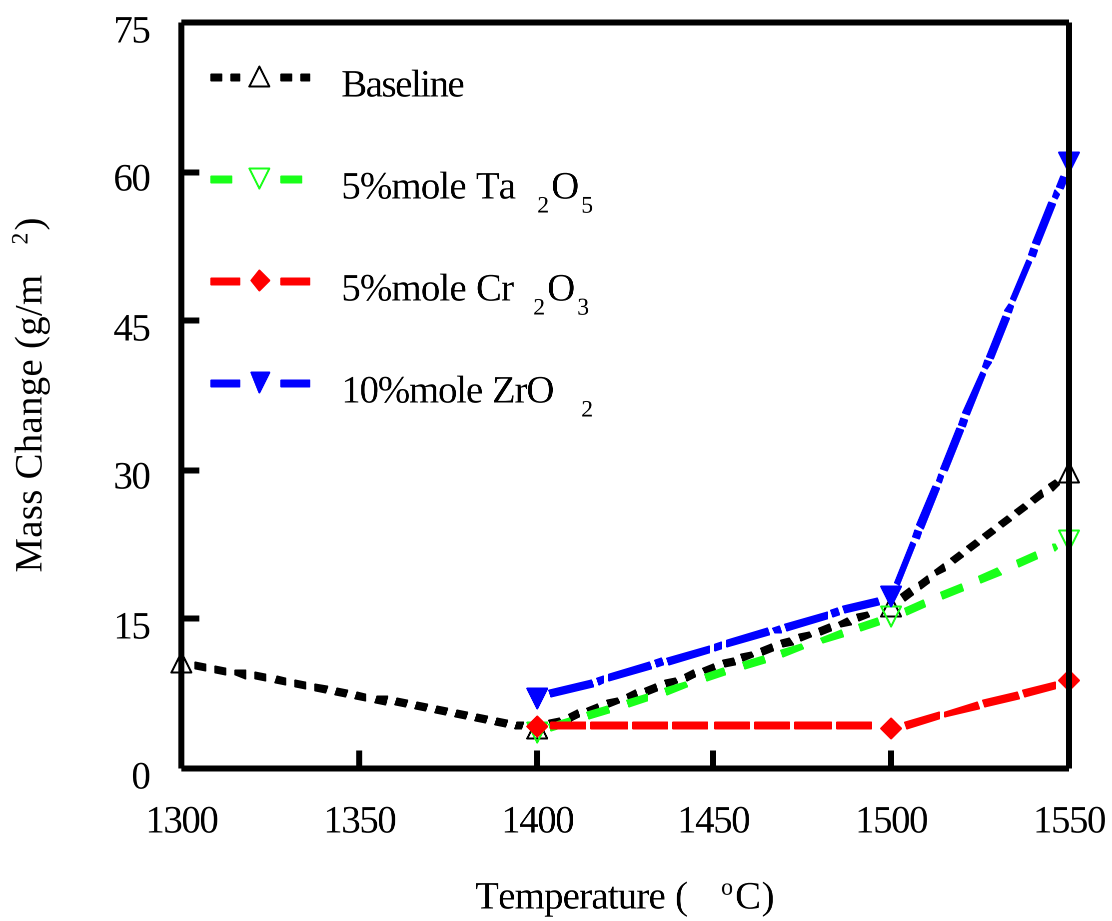
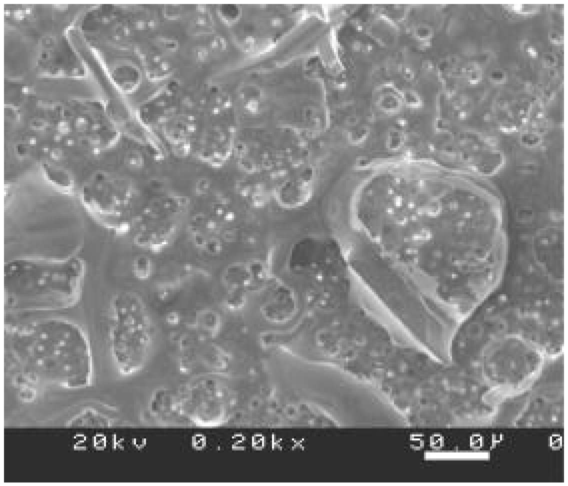
Oxidation of Si_3N_4 Ceramics Modified with CrB_2, TaB_2, ZrB_2, and BN



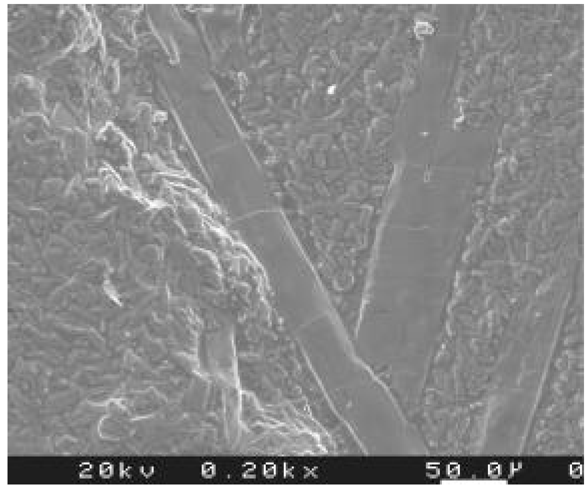
Oxidation of Si_3N_4 Modified with Cr_2O_3, Ta_2O_5, and ZrO_2



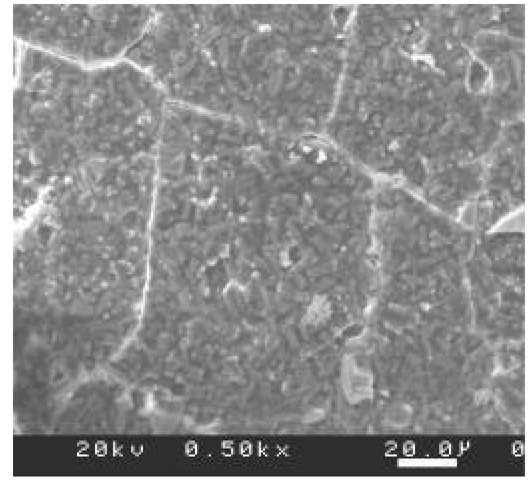
SEM of the Surface of the Modified $Si_3N_4/Y_2O_3+Al_2O_3$ Ceramics after Oxidation at 1500ºC for 2 Hours



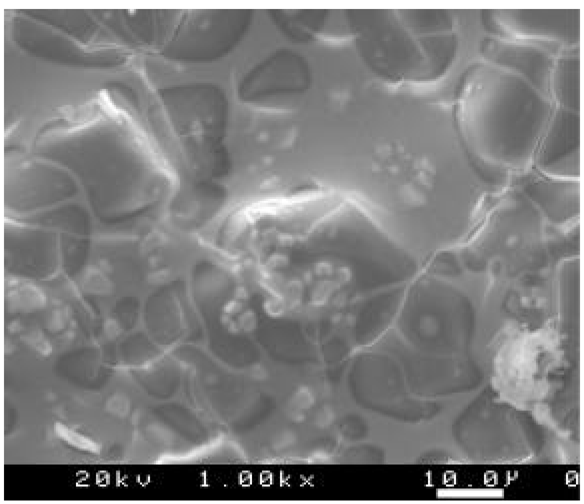
Baseline



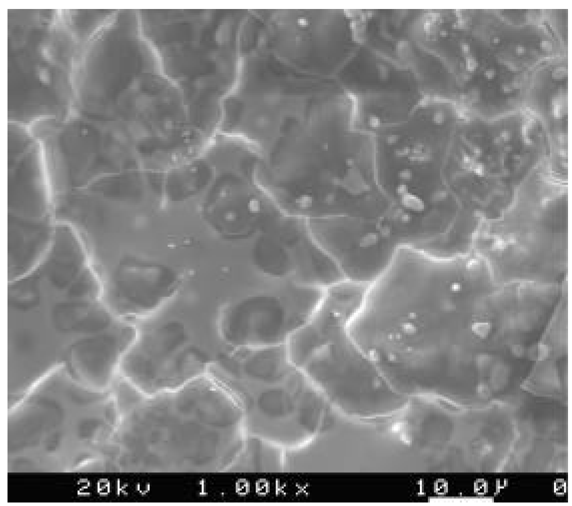
CrB_2



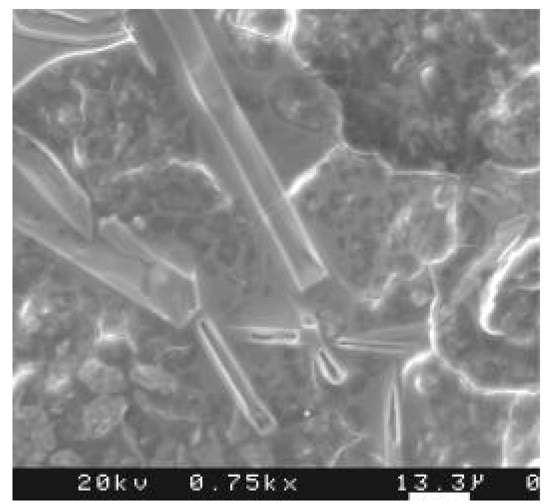
Cr_2O_3



TaB_2

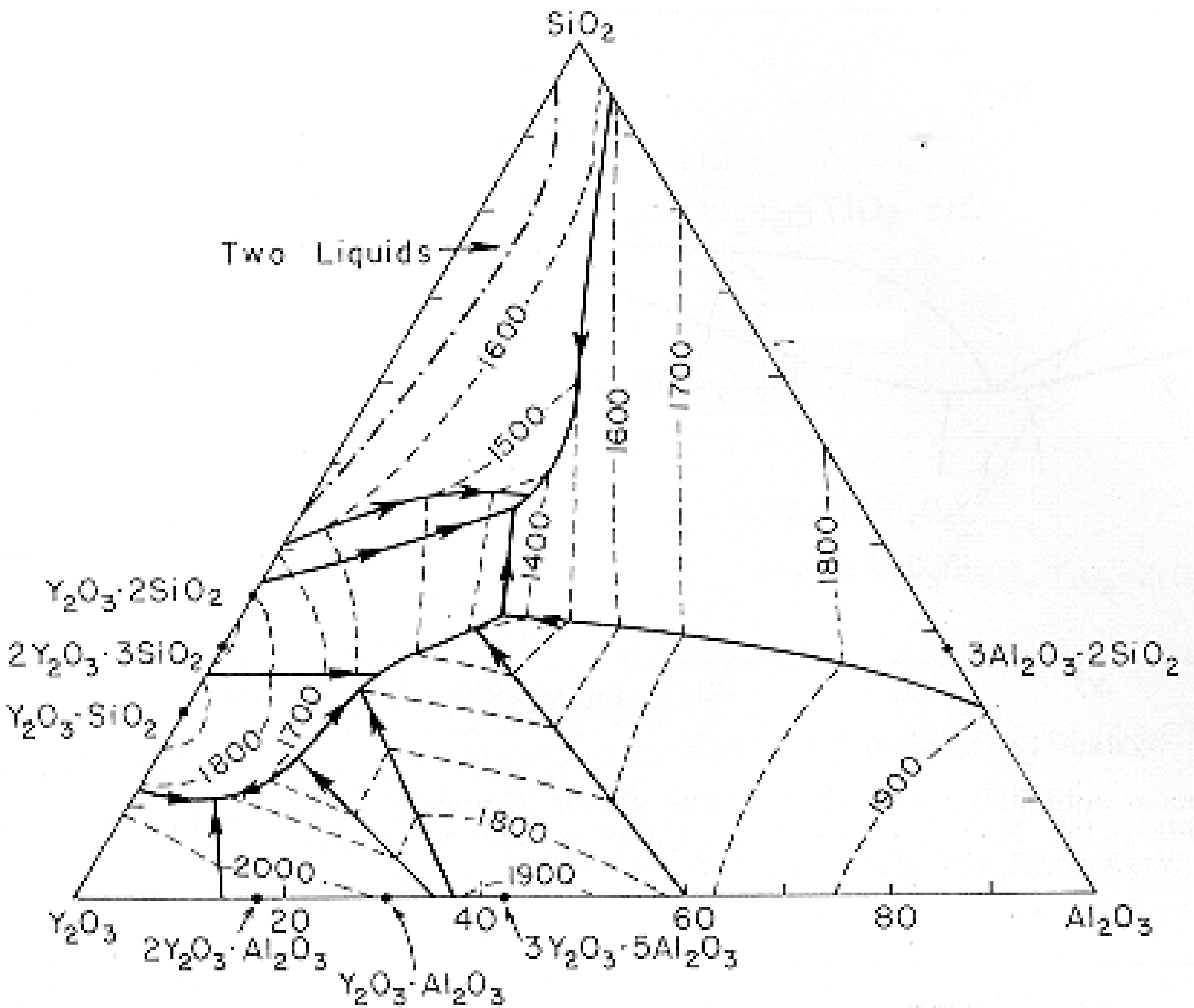


ZrB_2

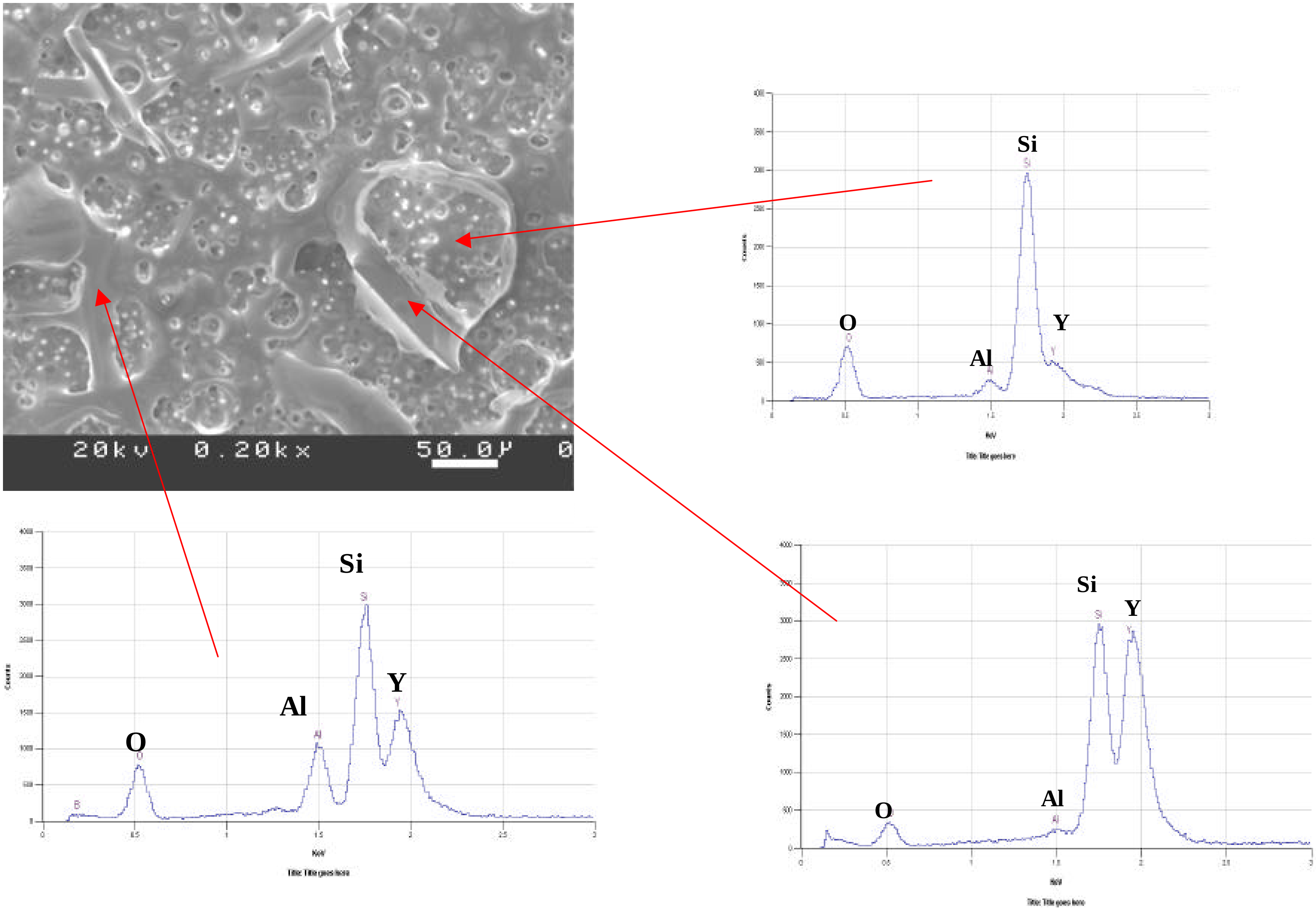


BN

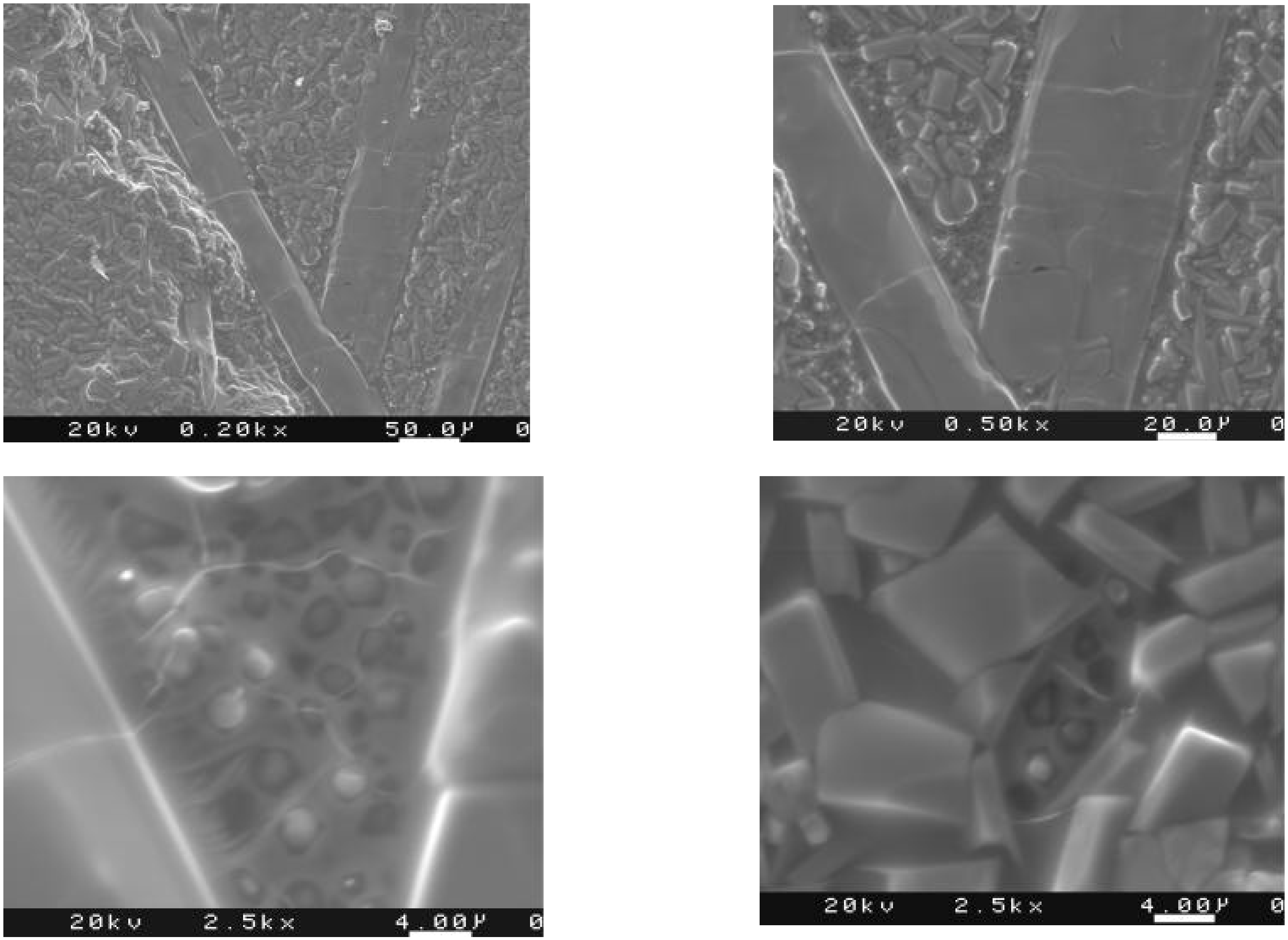
Phase Diagram of the System $Y_2O_3 – SiO_2$ - Al_2O_3



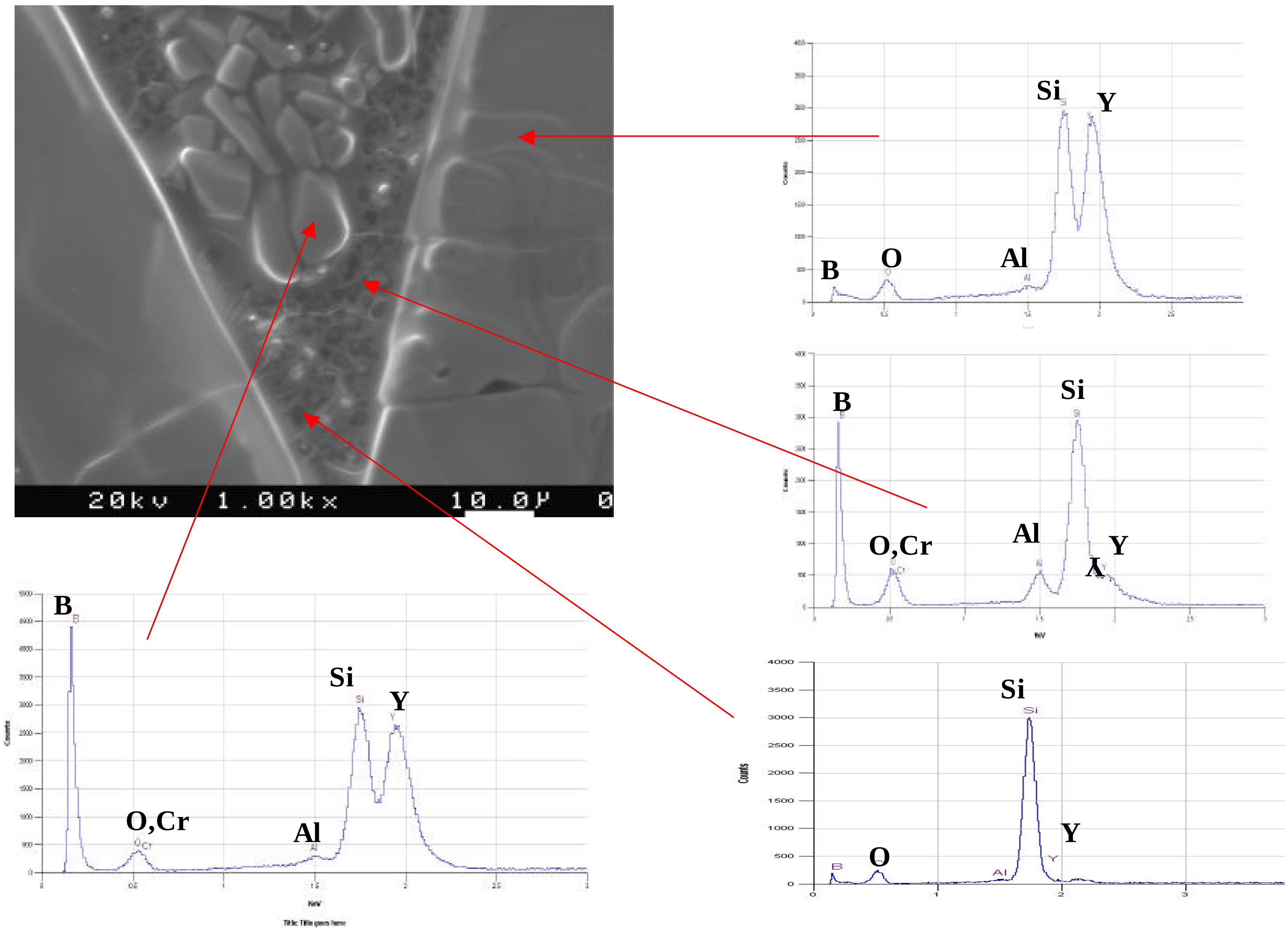
SEM and EDX Images of the Surface of the $Si_3N_4/Y_2O_3+Al_2O_3$ (Baseline) Ceramics after Oxidation at 1500°C for 2 Hours Showing Phase Separation in the Glass



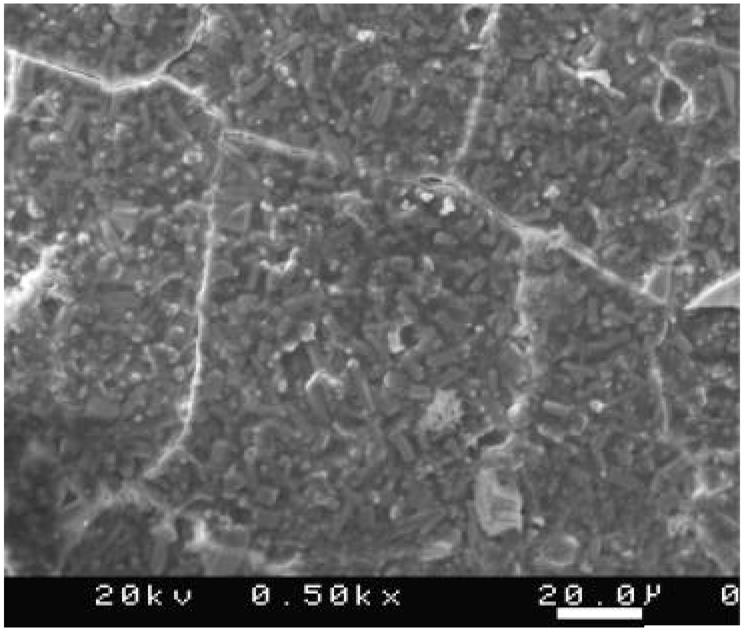
SEM Micrographs of the Crystallized Surface of $Si_3N_4/Y_2O_3+Al_2O_3$ Ceramics Modified with 10 mole % CrB_2 after Oxidation at 1500°C for 2 Hours

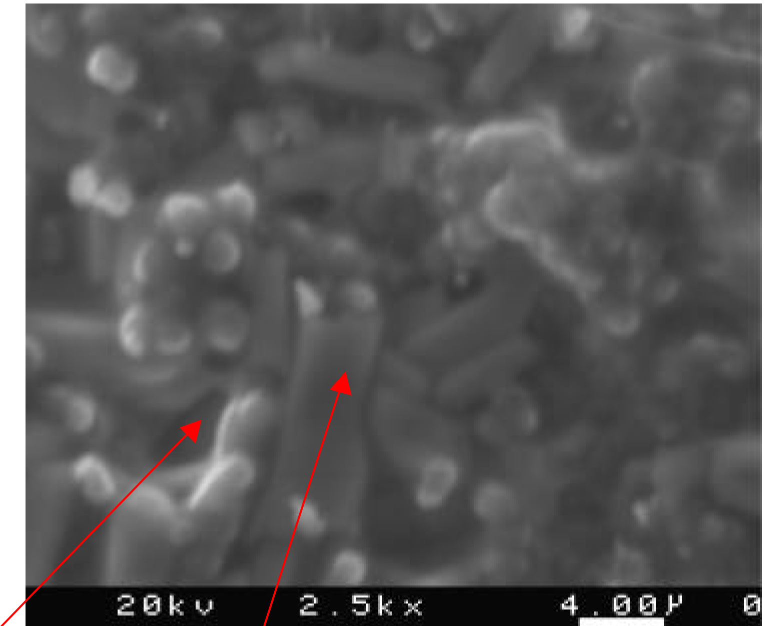


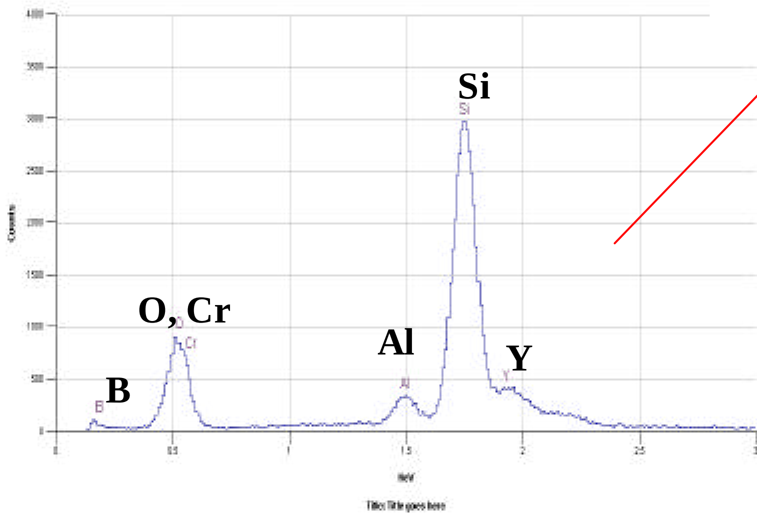
SEM and EDX of the Surface of $Si_3N_4/Y_2O_3+Al_2O_3$ Ceramics Modified with 10 mole% CrB_2 after Oxidation at 1500°C for 2 Hours Showing Phase Separation in the Glass

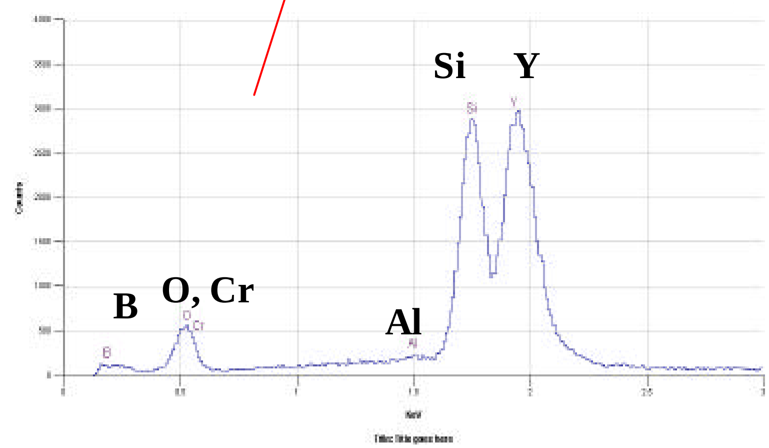


SEM and EDX of the Surface of $Si_3N_4/Y_2O_3+Al_2O_3$ Ceramics Modified with 5 mole % Cr_2O_3 after Oxidation at 1500ºC for 2 Hours









Phase Diagram of the System $Cr_2O_3 – SiO_2$

Cr_2O_3–SiO_2

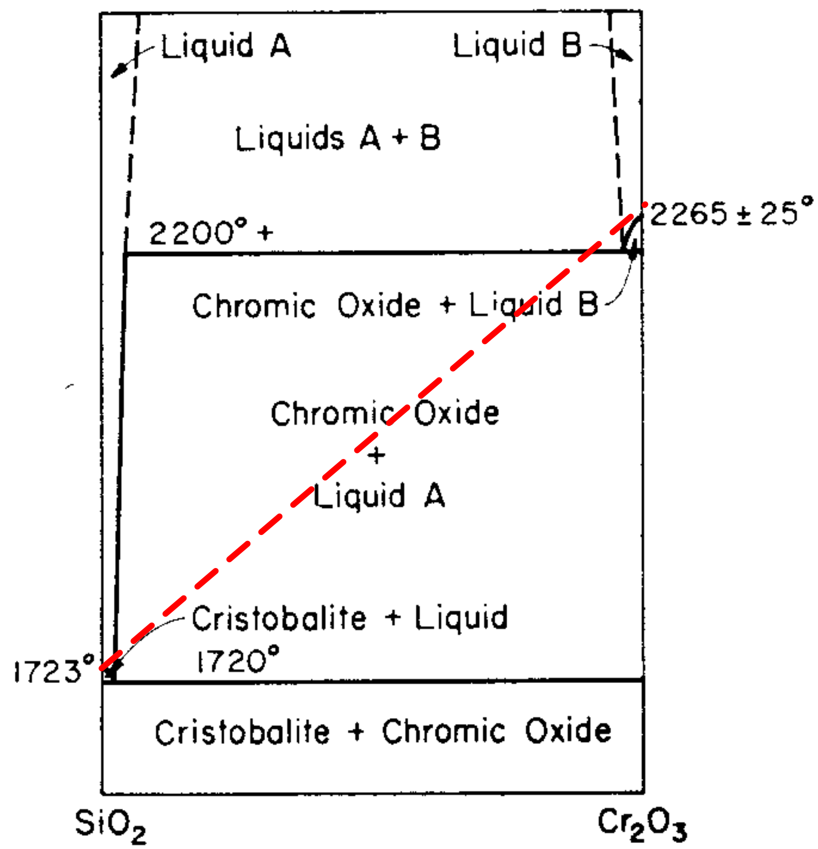


FIG. **332.**—System Cr_2O_3–SiO_2; probable.

From data of E. N. Bunting, *J. Research, Natl. Bur. Standards* **5** [2] 325–27 (1930), RP 203; and *ibid.*, **6** [6] 947–49 (1931), RP 317. M. L. Keith, *J. Am. Ceram. Soc.*, **37** [10] 490 (1954).

Relationship between Crystallization Parameters of Melt and Surface Tension

Rate of Nucleation, *I*

$$I = nv \exp\left[-(N/RT)(16\pi \bullet \sigma^3 / 3\Delta H_f^2)(T_m/\Delta T)^2\right] \exp\left[-\Delta E_D / RT\right]$$

where
- I = nuclei / ($cm^3 \cdot s$)
- n = number of atoms / cm^3
- v = atomic vibration frequency (s^{-1})
- N = Avogadro's number ($mole^{-1}$)
- R = Universal gas constant (J/(mole·K))
- σ = surface tension (J/cm^2)
- ΔH_f = heat of fusion (J/cm^3)
- T_m = melting temperature (K)
- ΔT = undercooling (K)
- ΔE_D = activation energy for atom to cross the "liquid-nucleus" interface (J/mole)

Critical Size of Nuclei, *r**

$$r^* = \frac{2 \bullet \sigma}{\Delta G_v}$$

where

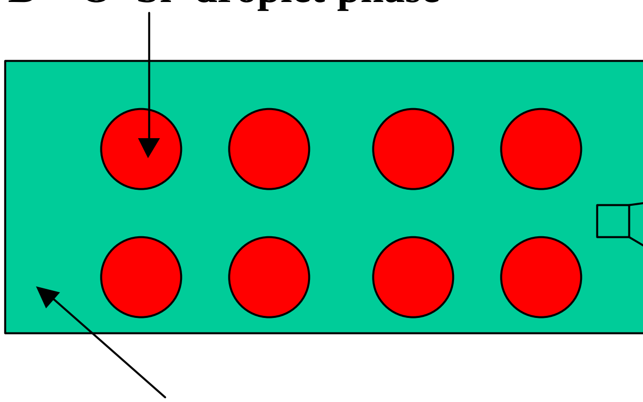
- r^* = critical radius (cm)
- σ = surface tension (J/cm^2)
- ΔG_v = free energy of crystallization (J/cm^3)

Arun K. Varshneya, "Fundamentals of inorganic Glasses", Academic Press, Inc., 1994, 45-48

The Role of Cr_2O_3 in the Formation of the Surface Structure of CrB_2 - and Cr_2O_3 - Modified $Si_3N_4/Y_2O_3+Al_2O_3$ Ceramics

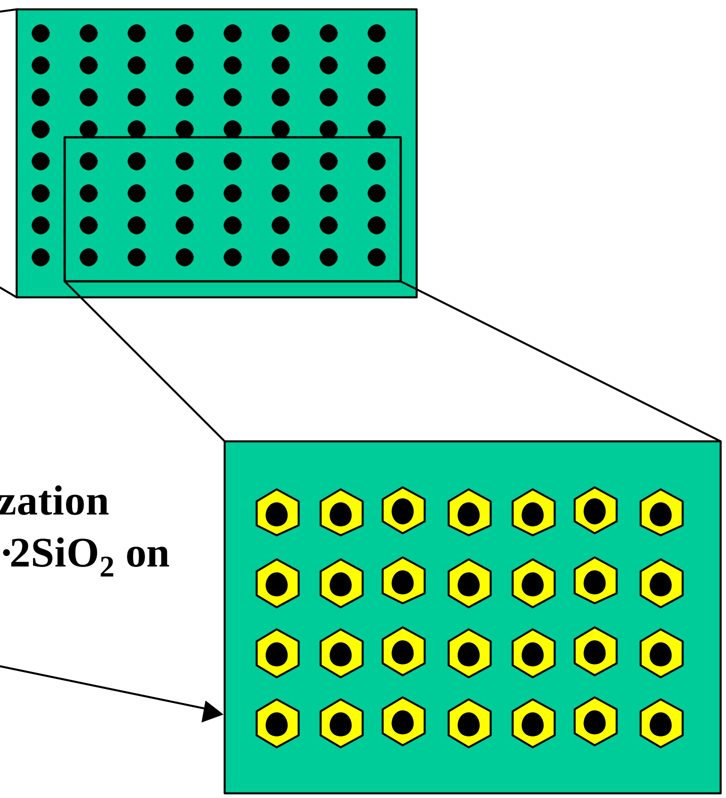
Step 1: **Phase separation in the surface melt**

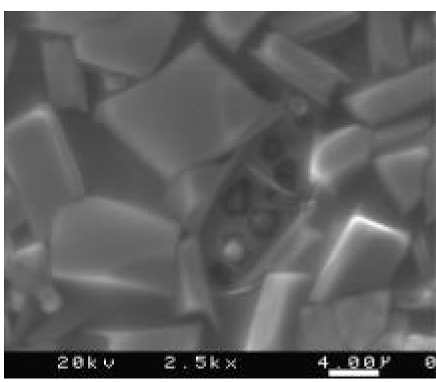
B – O- Si droplet phase



Si – Y – Al – Cr – B – O matrix phase

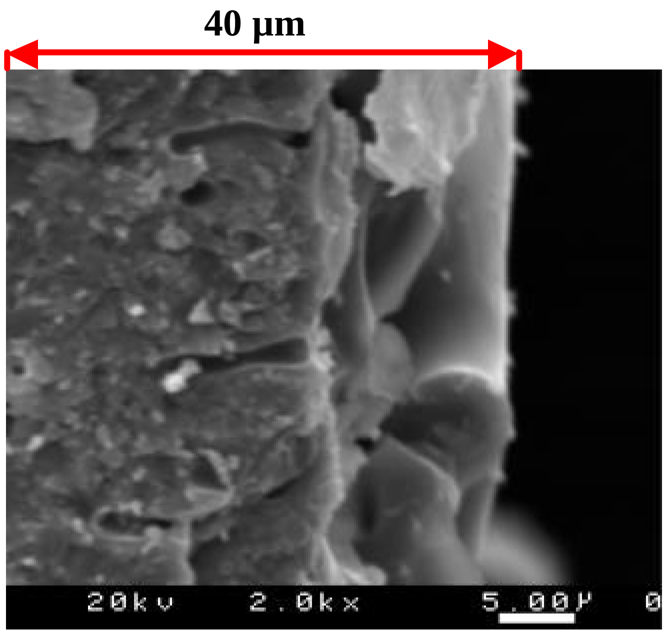
Step 2: **Homogeneous nucleation and formation of Cr_2O_3 crystallization centers in the matrix phase.**



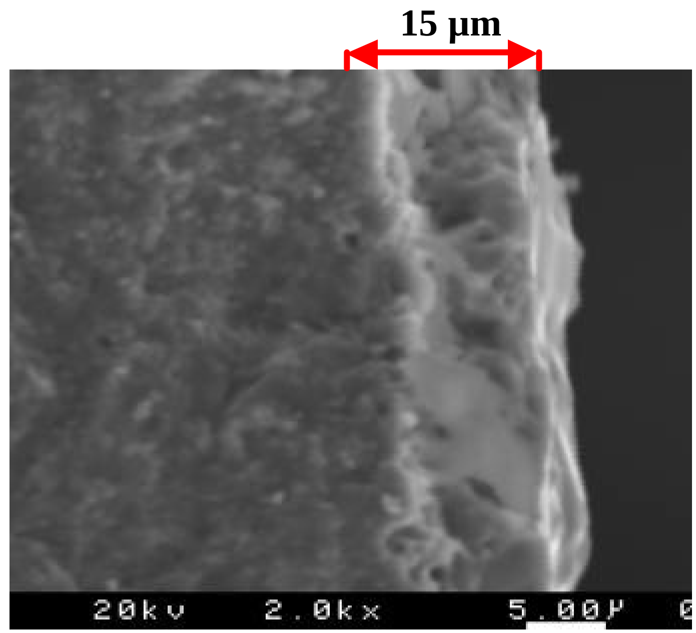


Step 3: **Catalytic crystallization (epitaxial growth) of $Y_2O_3{\cdot}2SiO_2$ on Cr_2O_3 centers**

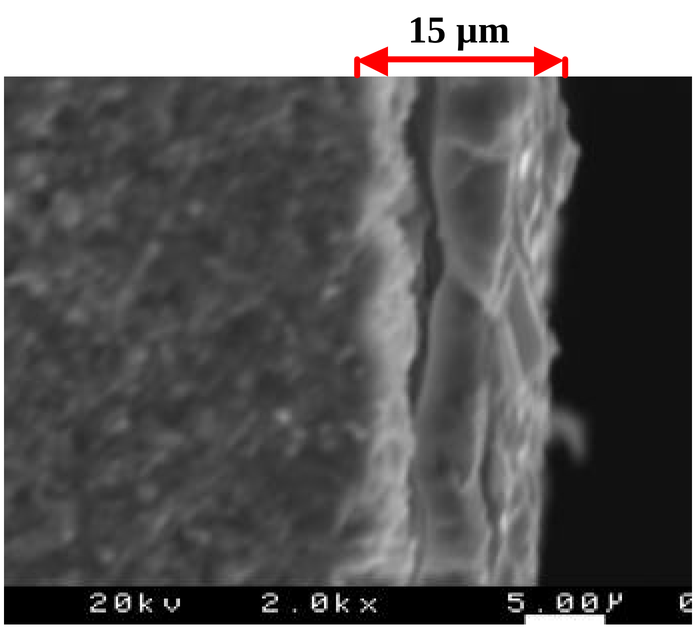
Thickness of the Oxidized Layer of the Modified $Si_3N_4/Y_2O_3+Al_2O_3$ Ceramics



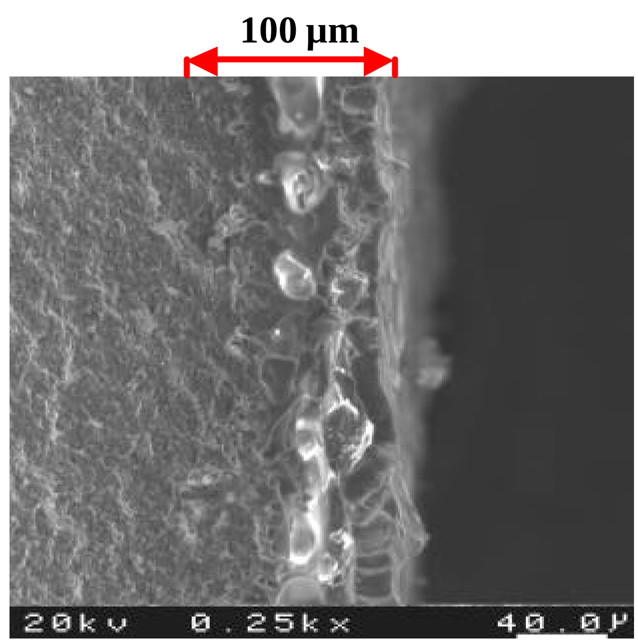
Baseline



CrB_2



Cr_2O_3

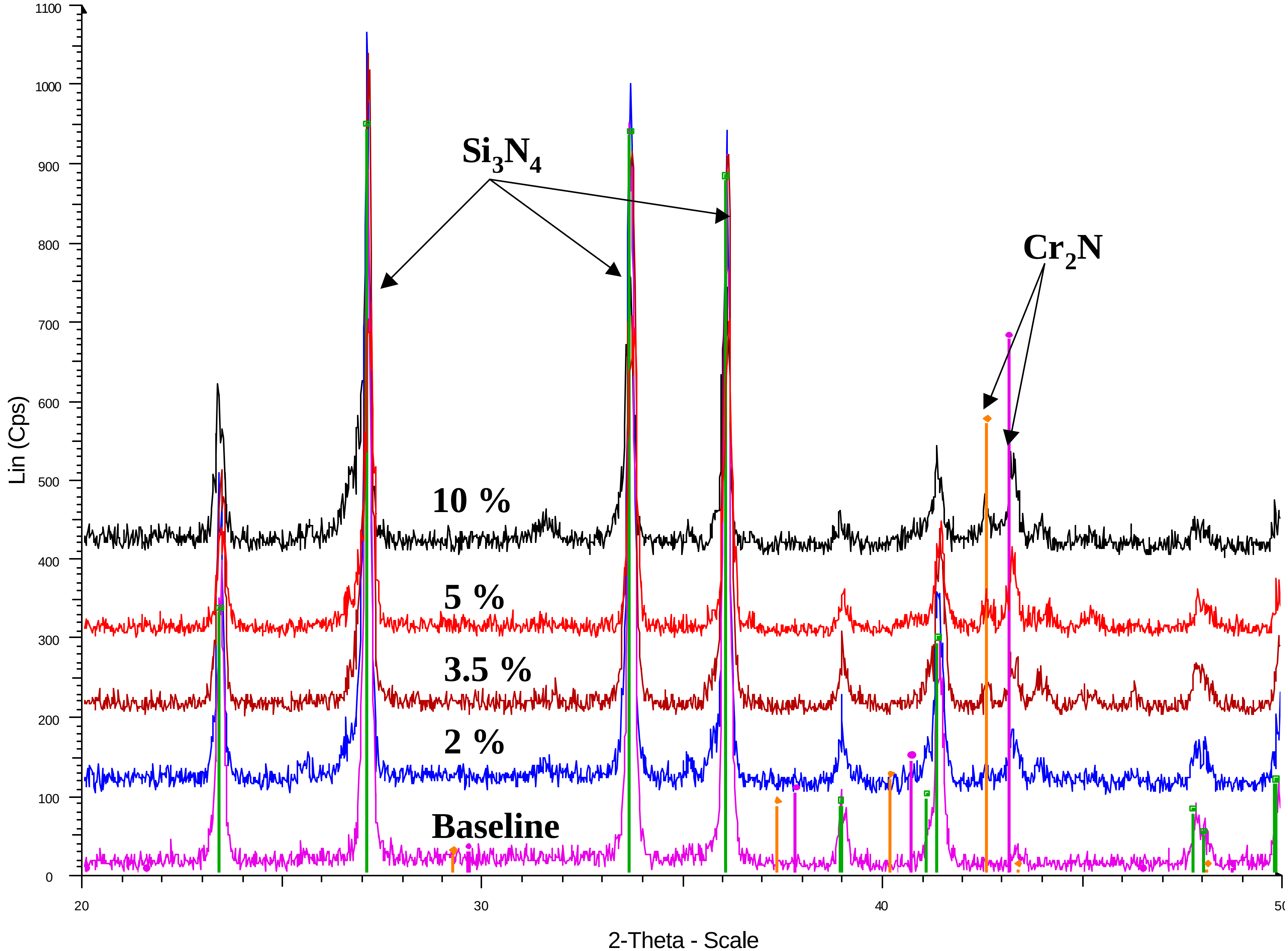


BN

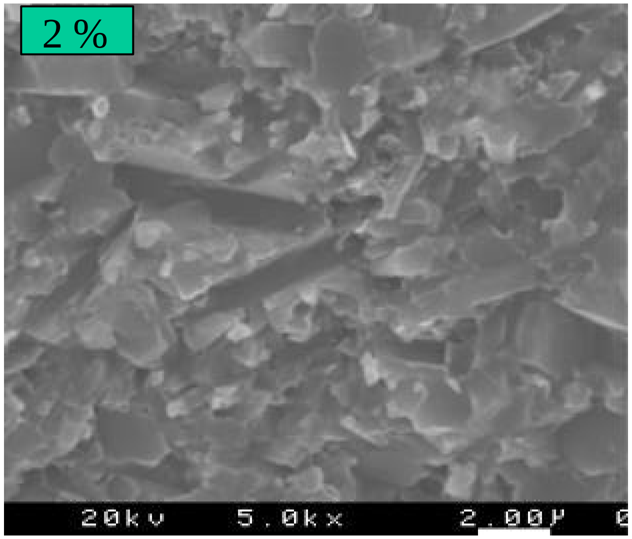
Effect of CrB_2 Content

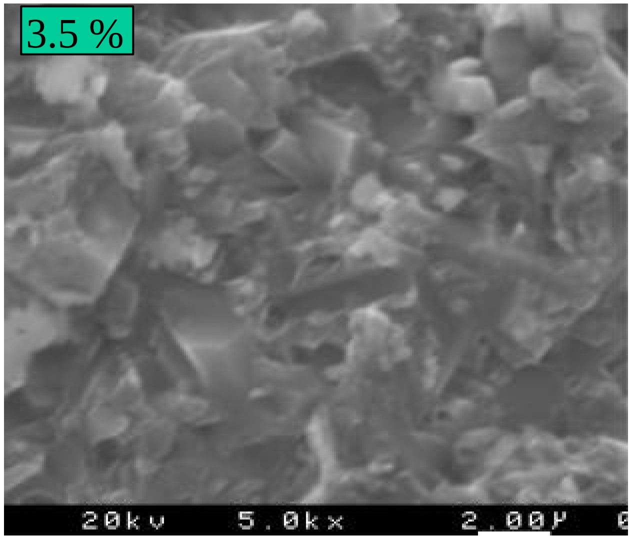
2, 3.5, 5, and 10 volume %

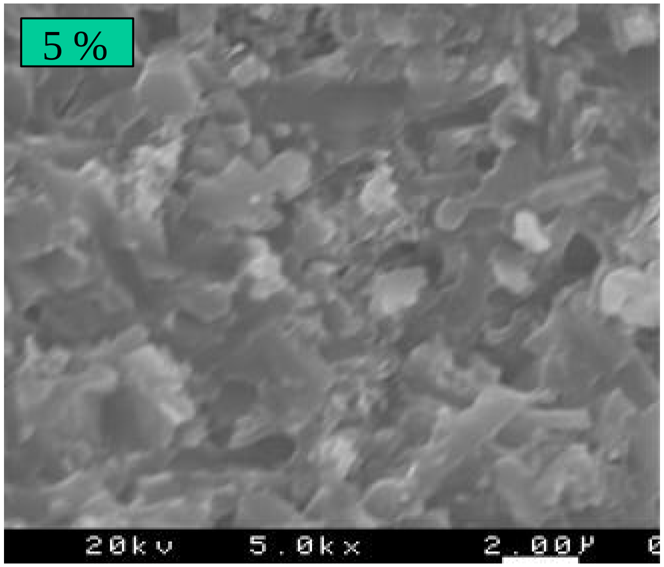
XRD of Si_3N_4 (5 wt.% Y_2O_3, 2 wt. % Al_2O_3) Ceramics Containing 0 – 10 vol. % CrB_2

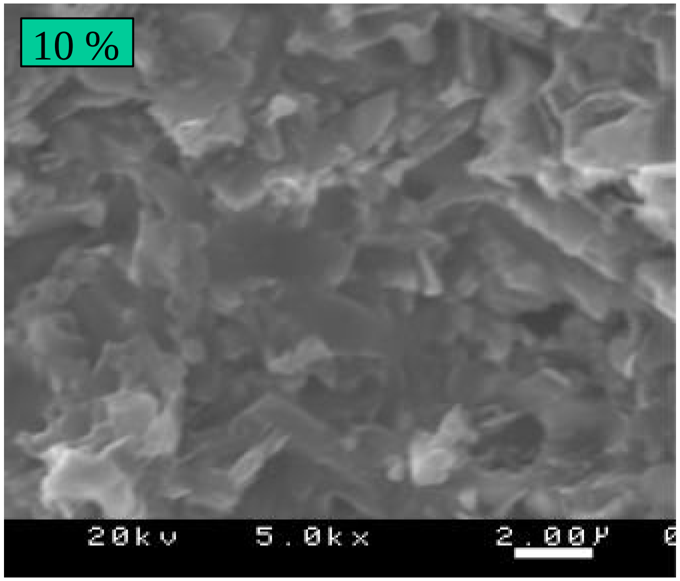


SEM Micrographs of the $Si_3N_4/Y_2O_3+Al_2O_3$ Ceramics Modified with 2 - 10 vol. % CrB_2



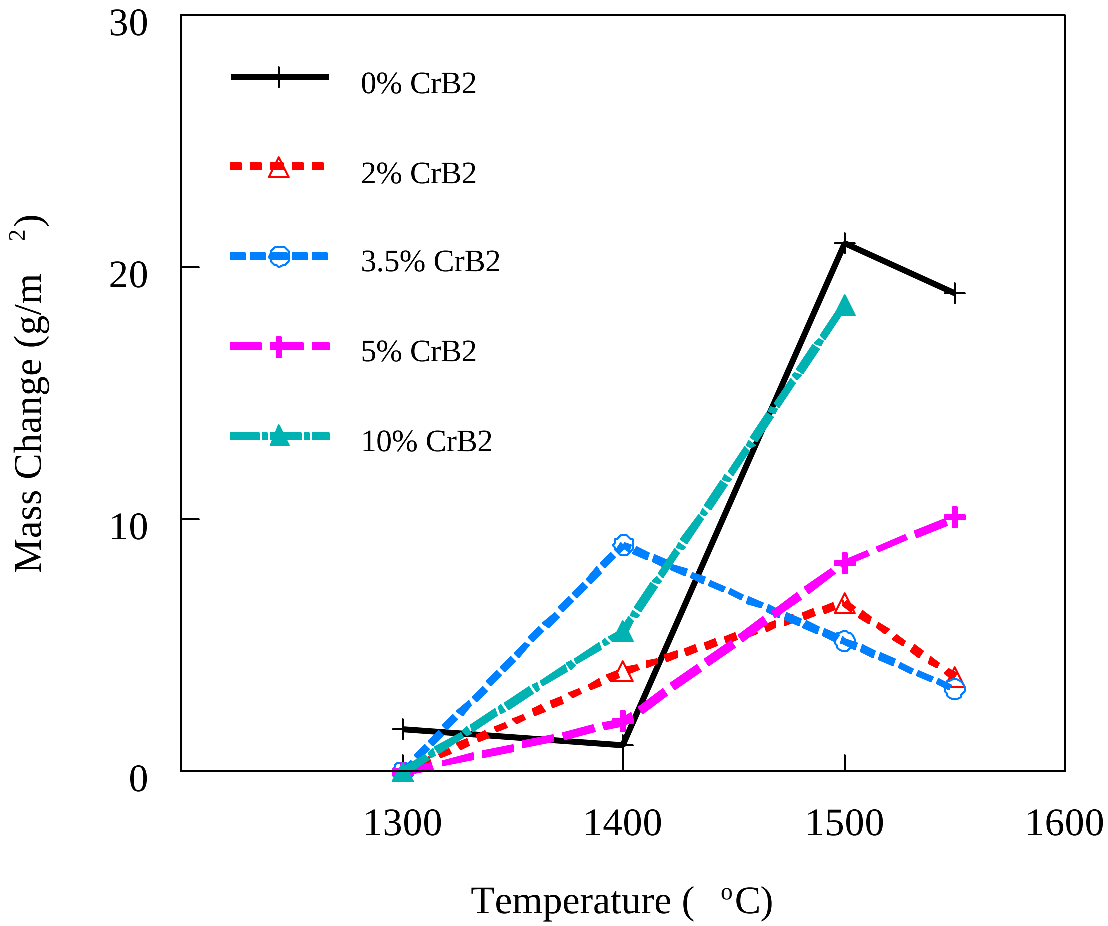






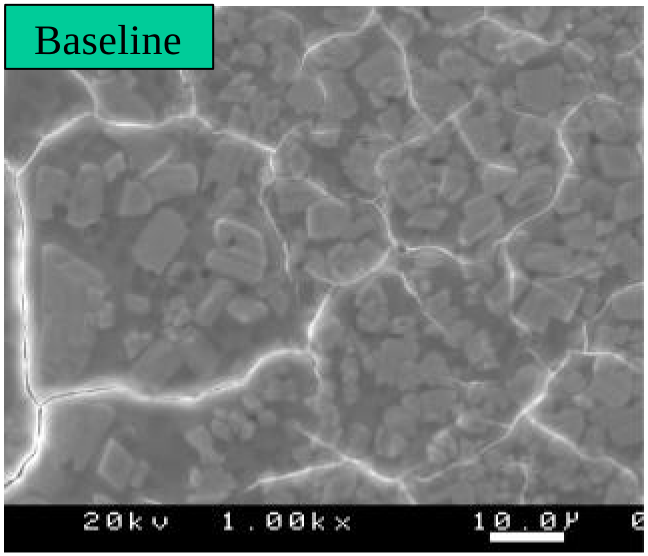
Oxidation of Si_3N_4 (Y_2O_3/Al_2O_3) Ceramics

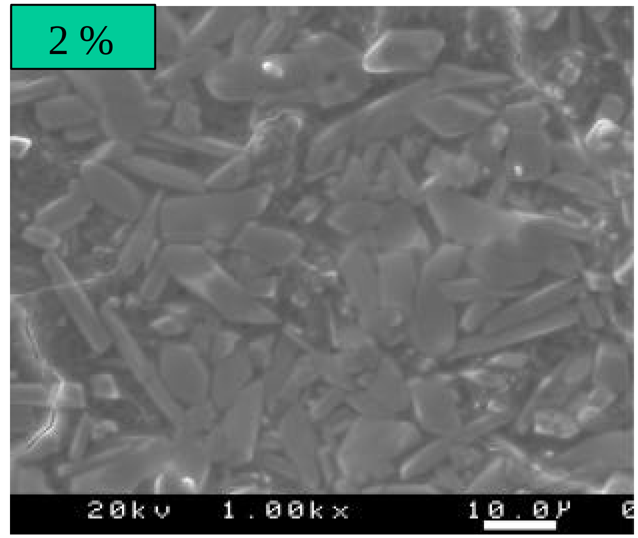
As a Function of CrB_2 Content (in vol. %) and Temperature (2 h hold)

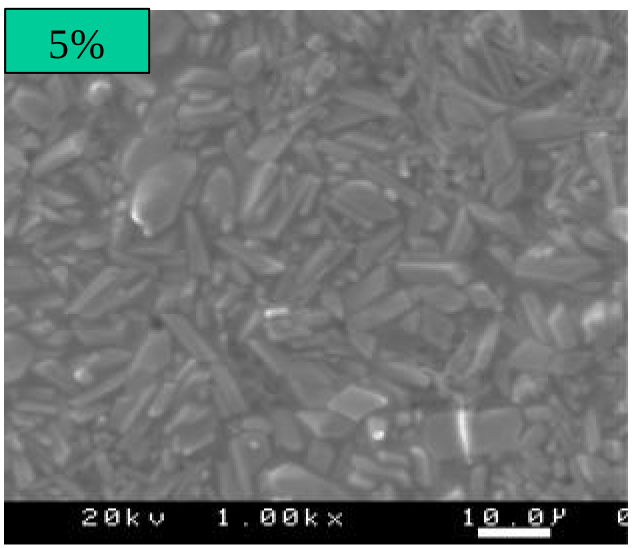


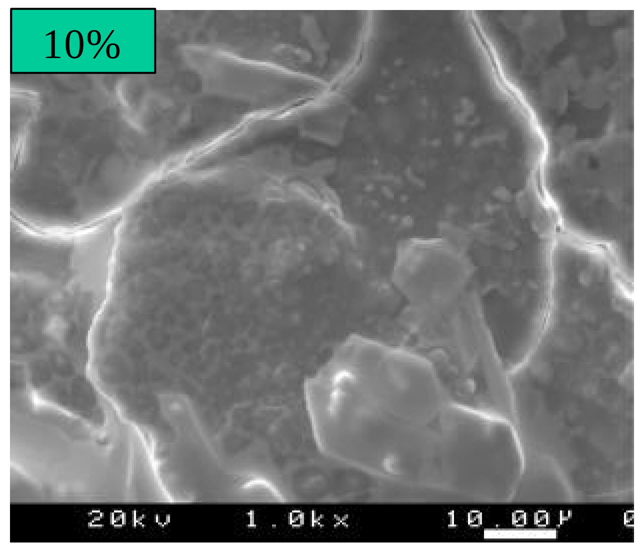
SEM Micrographs of the Surface of Si_3N_4 Ceramics

Containing 0 – 10 vol.% CrB_2 After Oxidation at 1400°C for 2 hours

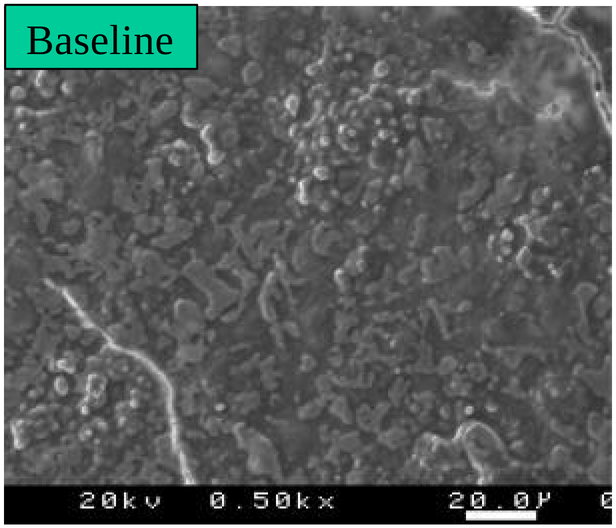


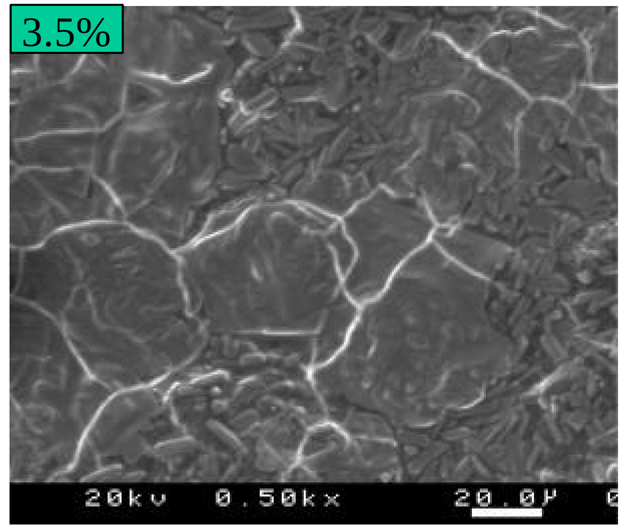


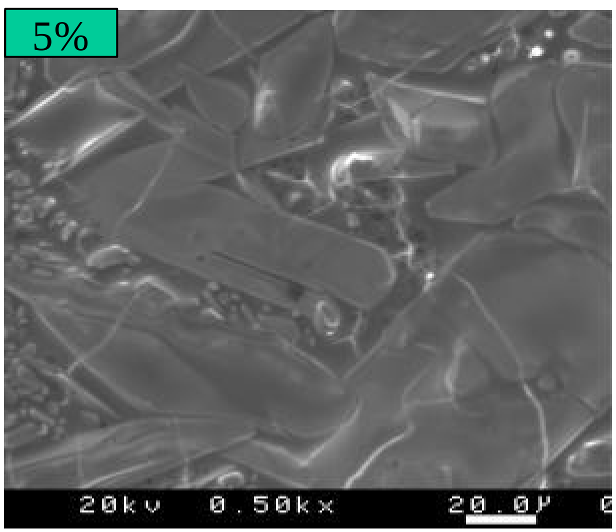


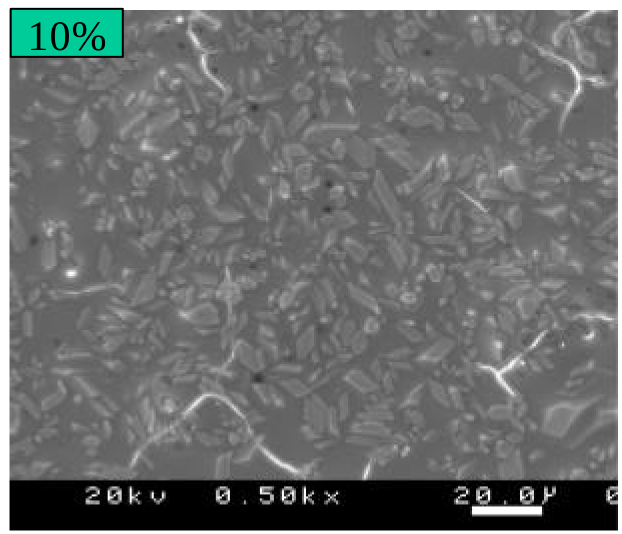


SEM Micrographs of the Surface of Si_3N_4 Ceramics Containing 0 – 10 vol.% CrB_2 After Oxidation at 1400°C for 10 hours

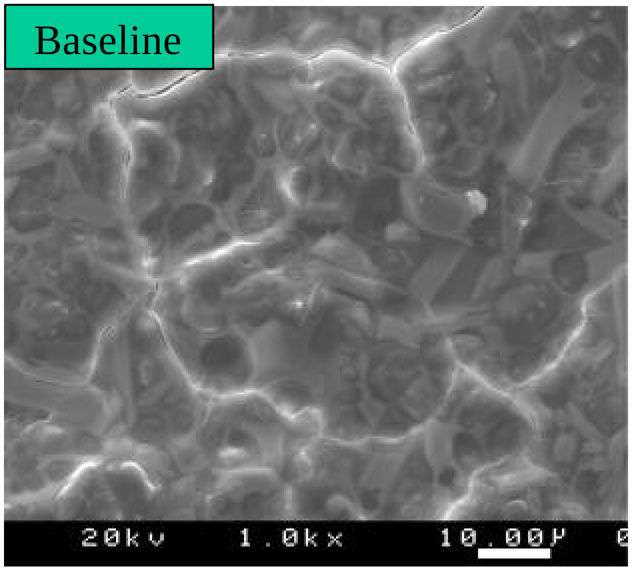


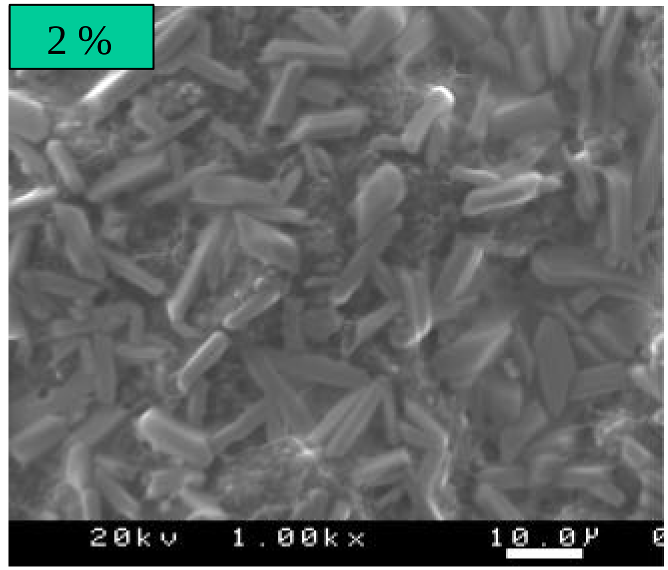


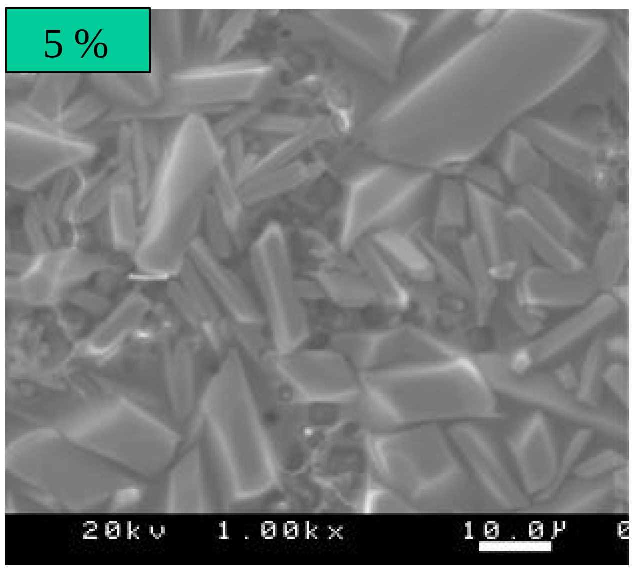




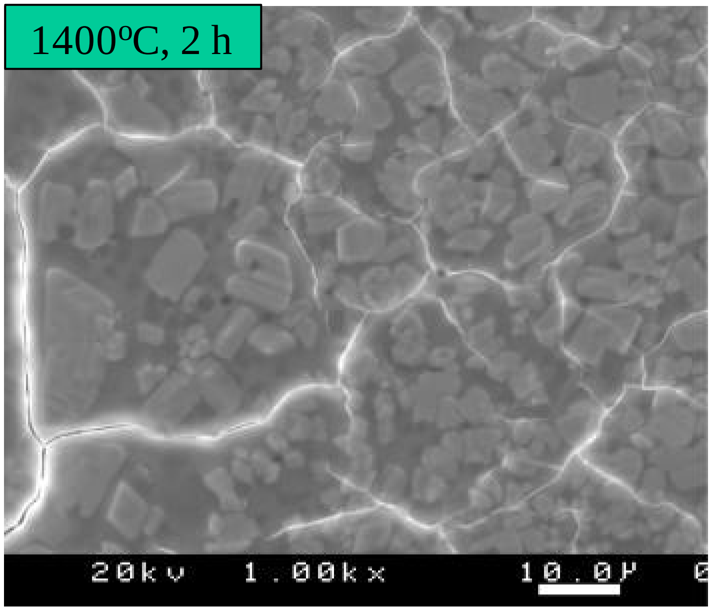
SEM Micrographs of the Surface of Si_3N_4 Ceramics Containing 0 –5vol.% CrB_2 After Oxidation at 1550°C for 2 hours

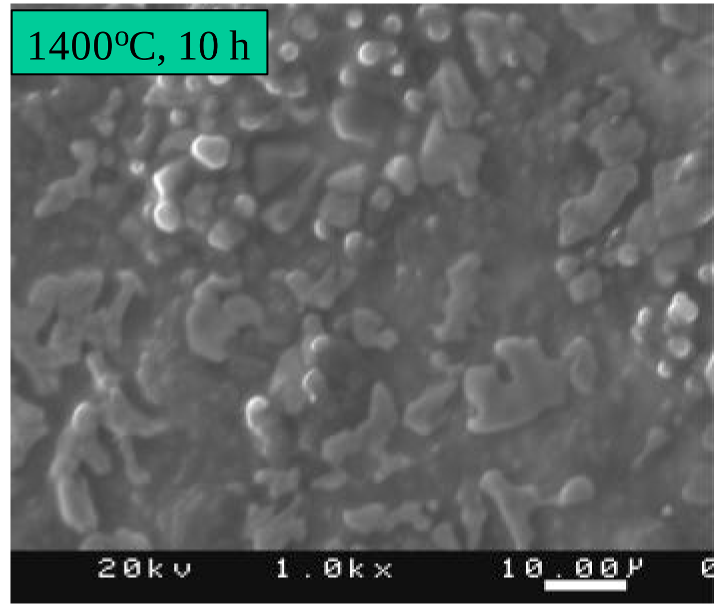


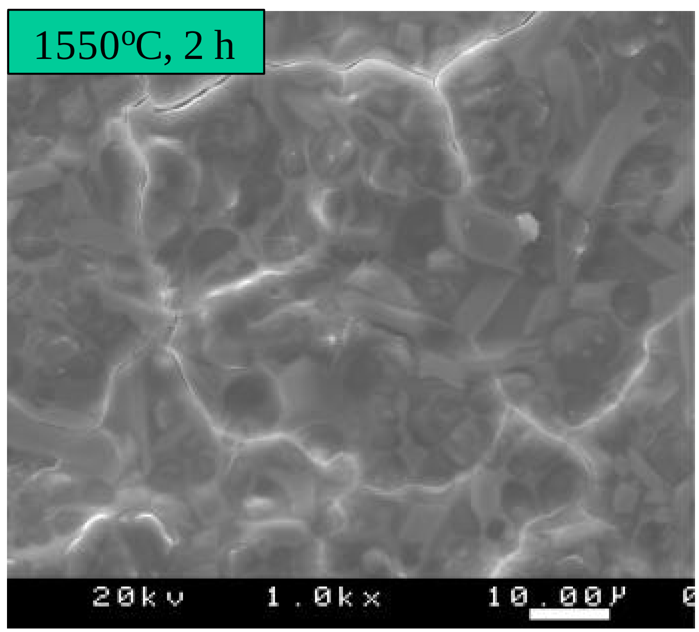




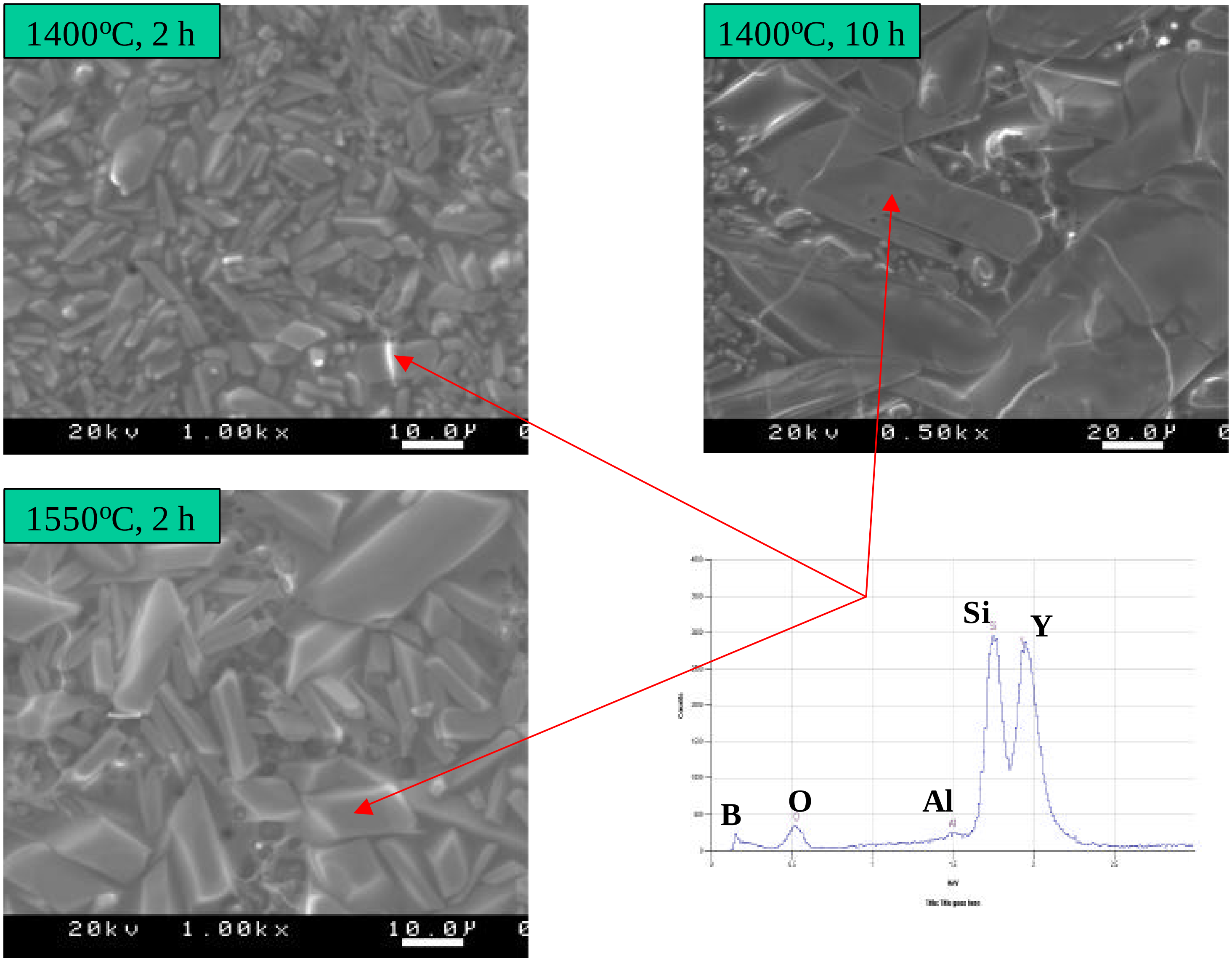
SEM Micrographs of the Oxidized Surface of the Baseline Si_3N_4 Ceramics



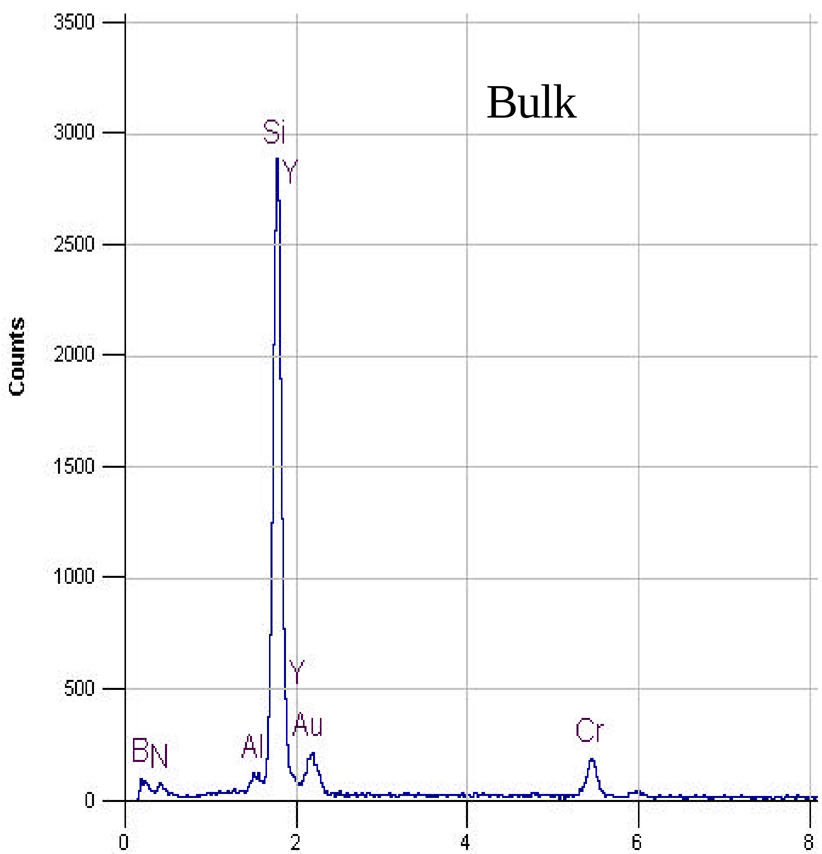


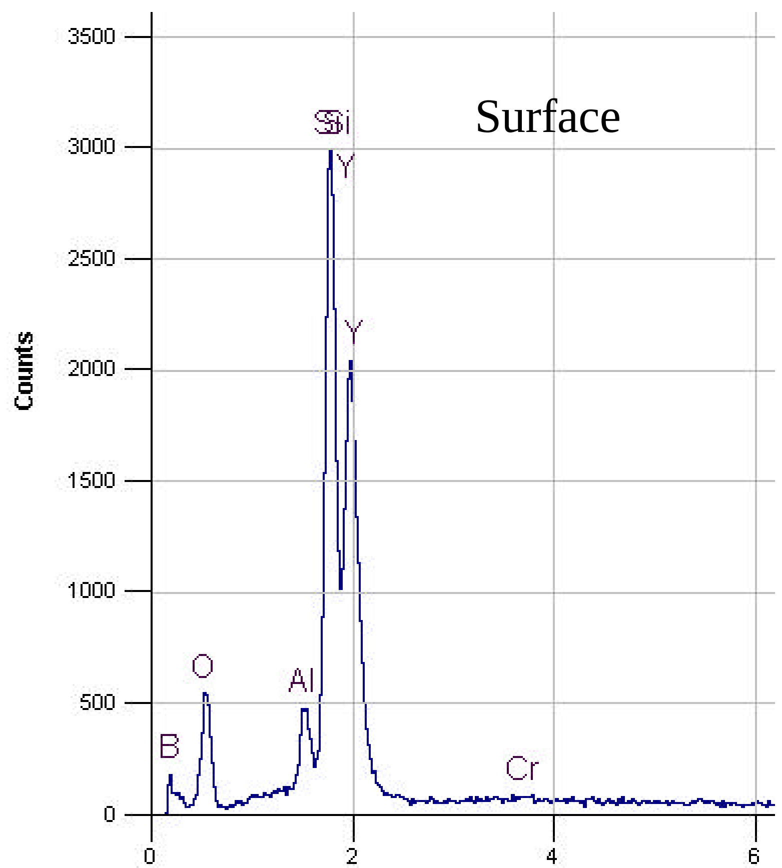


SEM Micrographs of the Oxidized Surface of Si_3N_4 Ceramics Containing 5 vol.% CrB_2



EDX of the Bulk and Oxidized Surface of Si_3N_4 Ceramics Containing 5 vol.% CrB_2





Summary

- The oxidation resistance of Si_3N_4 /2 wt.%Al_2O_3+5 wt.%Y_2O_3 modified with Cr, Ta, and Zr diborides and oxides and BN was studied as a function of the composition and structure of the oxidized surface layer.

- Baseline ceramics exhibited phase separation in the surface melt with the formation of yttria-rich matrix phase and silica-rich droplets.

- Only the introduction of CrB_2 or Cr_2O_3 led to an increase in the oxidation resistance of Si_3N_4 ceramics in air up to 1550°C.

- A change in the CrB_2 content affected significantly the structure the protective layer. The highest oxidation resistance was shown by the ceramics containing below 5 vol. % CrB_2.

- The presence of Cr_2O_3 in the surface melt induced its extensive immiscibility and catalyzed in-situ crystallization of $Y_2O_3 \cdot 2SiO_2$ with melting (decomposition) temperature of 1775°C, which provided effective oxidation protection.