Oxidation of ZrB_2 SiC $TaSi_2$ Materials at Ultra High Temperatures

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ZrB_2 - 20v% SiC - 20v% $TaSi_2$ was oxidized in stagnant air for ten minute cycles for times up to 100 minutes at 1627°C and 1927°C. The sample oxidized at 1627°C showed oxidation resistance better than that of the standard ZrB_2 - 20v% SiC. The sample oxidized at 1927°C, however, showed evidence of liquid phase formation and complex oxidation products. The sample exposed at 1927°C was analyzed in detail by scanning electron microprobe and wavelength dispersive spectroscopy to understand the complex oxidation and melting reactions occurring during exposure. The as hot-pressed material shows the formation of a $Zr(Ta)B_2$ phase in addition to the three phases in the nominal composition already noted. After oxidation, the $TaSi_2$ in the matrix was completely reacted to form Ta(Zr)C. The layered oxidation products included SiO_2, ZrO_2, Ta_2O_5, and a complex oxide containing both Zr and Ta. Likely reactions are proposed based on thermodynamic phase stability and phase morphology.

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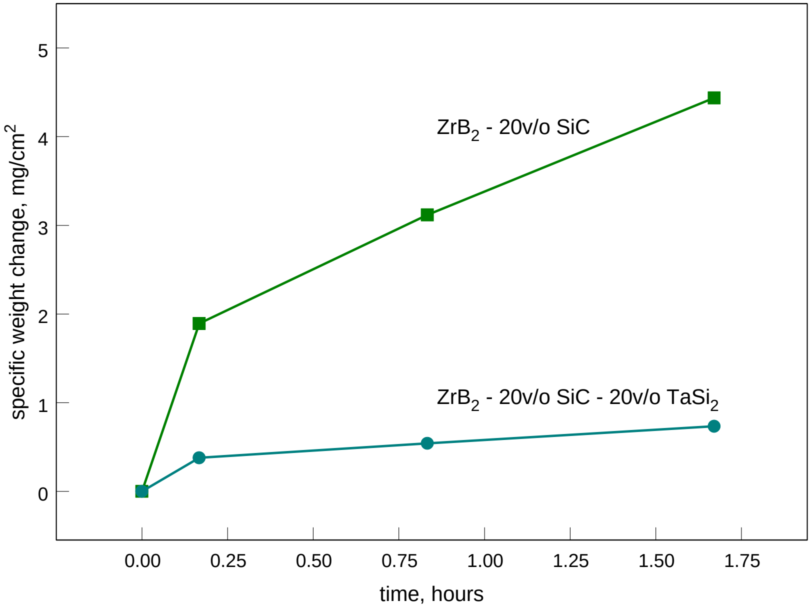
Background

- Previous work

  "Oxidation of ZrB_2- and HfB_2-based ultra-high temperature ceramics: effect of Ta additions," E. Opila, S. Levine, J. Lorincz, J. Mat. Sci. 39 [19] 5969-5977 (2004).
- Improved oxidation resistance with 20 v/o$TaSi_2$ additions to ZrB_2 - 20 v/o SiC at 1627°C in air up to 100 minutes
- Improved oxidation resistance attributed to Ta additions, not excess Si
- Oxidation at 1927°C resulted in excess liquid phase formation and poor oxidation resistance

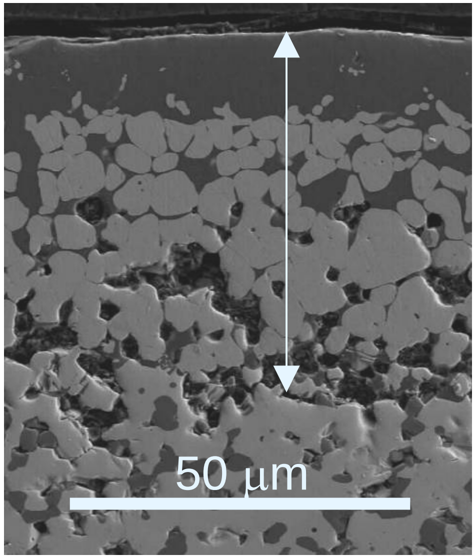
ZrB_2 - 20v/o SiC - 20v/o $TaSi_2$ showed improved oxidation resistance at 1627°C in air



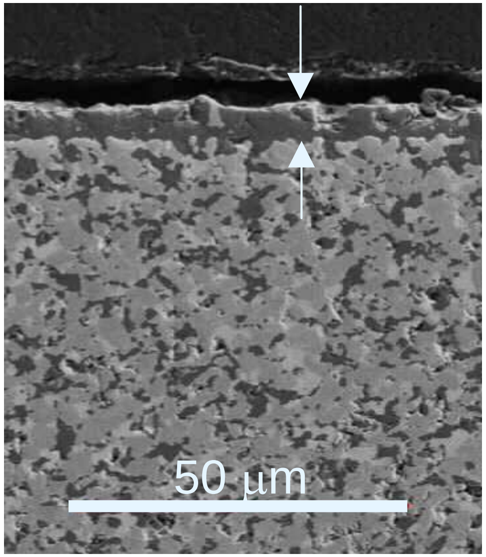
oxidized in 10 minute cycles

ZS: 1, 5, and 10 cycles

ZS20TS: 1, 5, and 10 cycles

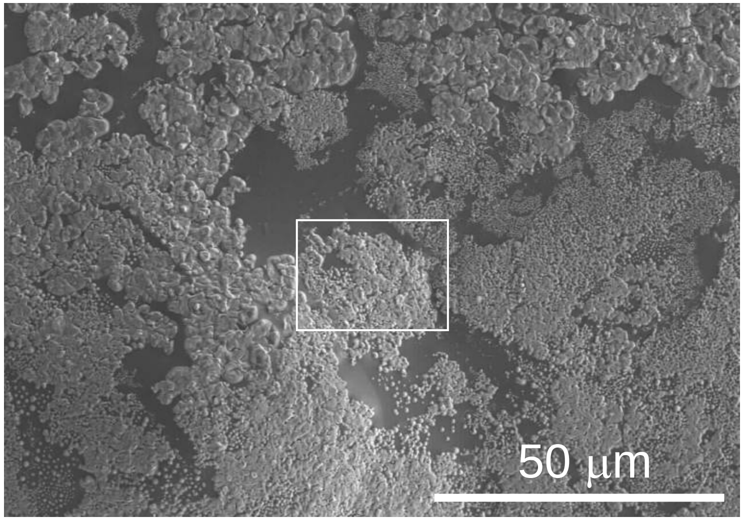


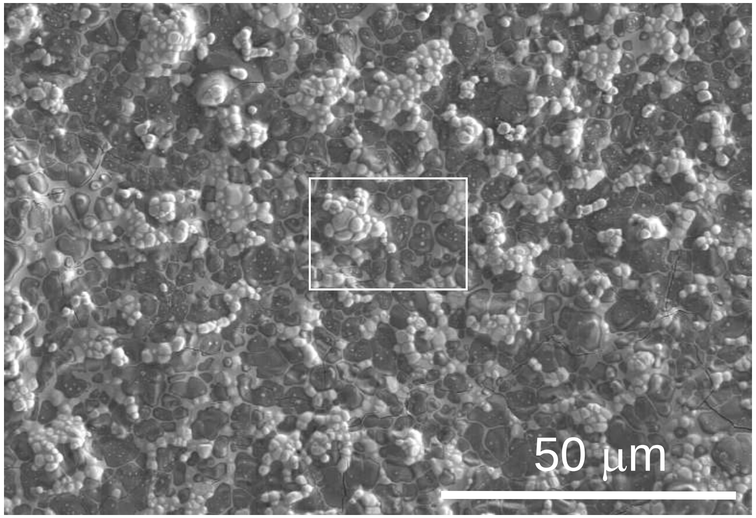
ZrB_2 – 20v/o SiC



ZrB_2 – 20v/o SiC – 20v/o $TaSi_2$

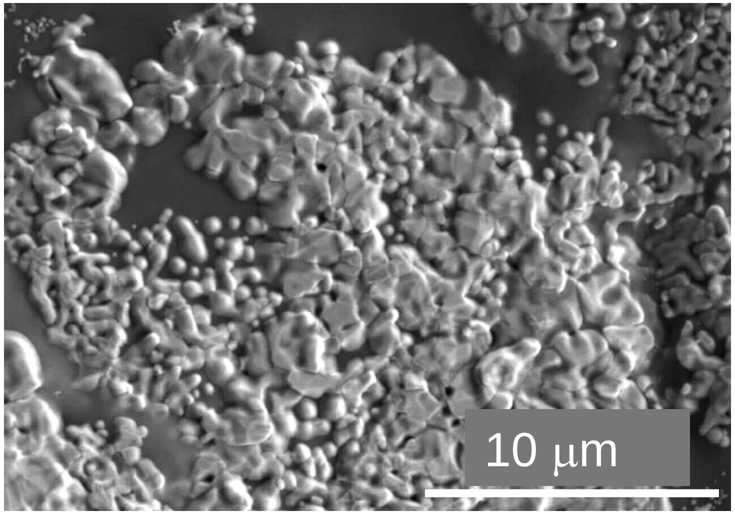
Surface oxide morphology, 1627°C, 100 min, air

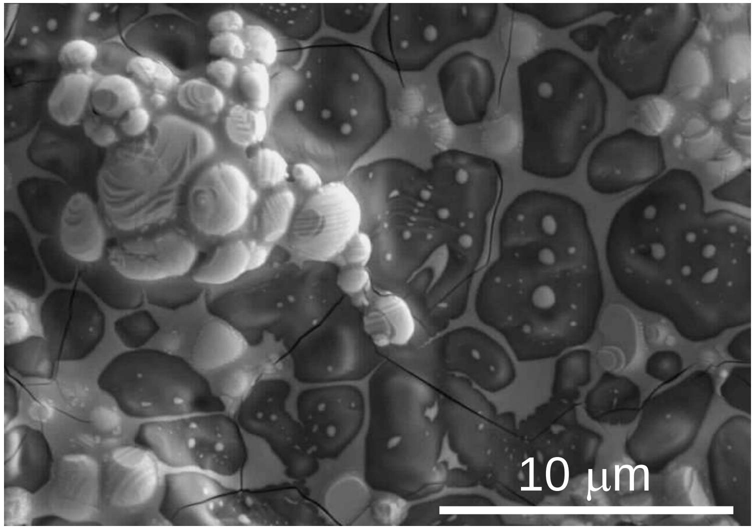




ZS

ZS20TS





Melt formation observed after ZS20TS oxidation at 1927°C in stagnant air

ZSTS: as-fabricated and 1 cycle

ZSTS: 5 cycles

Liquid phase formation a problem

- SiO_2: T_m=1723°C
- Ta_2O_5: T_m=1887°C
- $Ta_2O_5 \cdot 6ZrO_2$: T_m>1870°C

ZrO_2 provides some dimensional stability

ZS: 1, 5, and 10 cycles

Questions arising from 1927°C exposure

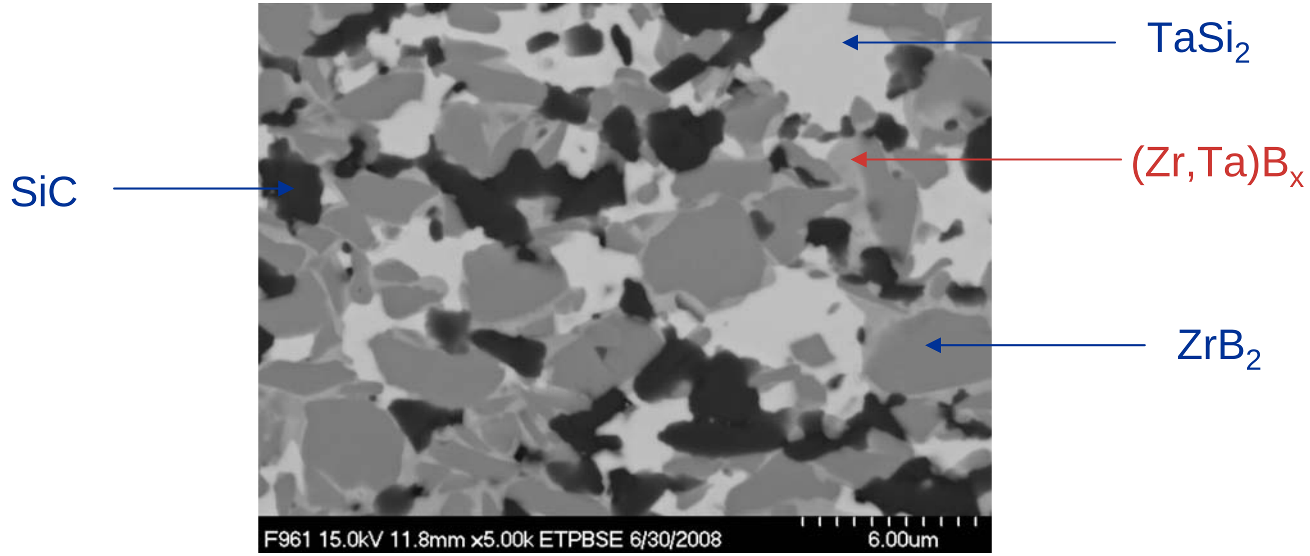
- Ta distribution in oxidation products
  - is all Ta contributing to melt formation?
  - any Ta in solid phases?
- What is the composition of oxidation products?
- Can liquid phase formation be limited while still retaining improved oxidation resistance at 1627°C?

Additional work since previous publication

- Characterization of ZS20TS after 1927°C, 5 x 10 min cycles in stagnant air
  - WDS/microprobe: JEOL 8200
  - FE-SEM: Hitachi S-4700
- Oxidation of ZS5TS at 1627°C, 1927°C for 1, 5 and 10 ten-minute cycles in stagnant air

Characterization of ZS20TS starting material

- Desired composition: ZrB_2 - 20v% SiC - 20v% $TaSi_2$
- As hot-pressed material shows 4 phases
  - Phase 1: ZrB_2 B/Zr = 1.97
  - Phase 2: SiC C/Si = 1.08
  - Phase 3: $TaSi_2$ Si/Ta = 2.16
  - Phase 4: $(Zr,Ta)B_x$ Zr/Ta = 4.19 B/(Zr+Ta) = 1.53



Stability of $TaSi_2$

ΔG_f 1927°C(kJ/mol) $M+X_x=MX_x$

$TaSi_2$	-61
TaC	-140
TaB_2	-191
$TaO_{2.5}$	-615
$ZrSi_2$	-141
ZrC	-180
ZrB_2	-285
ZrO_2	-741

- Silicides are least stable
- Zirconium compounds are more stable than tantalum compounds
- $(Zr,Ta)B_x$ formation: $TaSi_2$ reacts with excess B during hot pressing?

ZrB_2 TaB_2 solid solution?

- ZrB_2 and TaB_2 both hexagonal crystal structure
- Limited phase stability info found

Leitnaker, Bowman, Gilles,
J. Electrochem. Soc. 109 [5] 441 (1962).

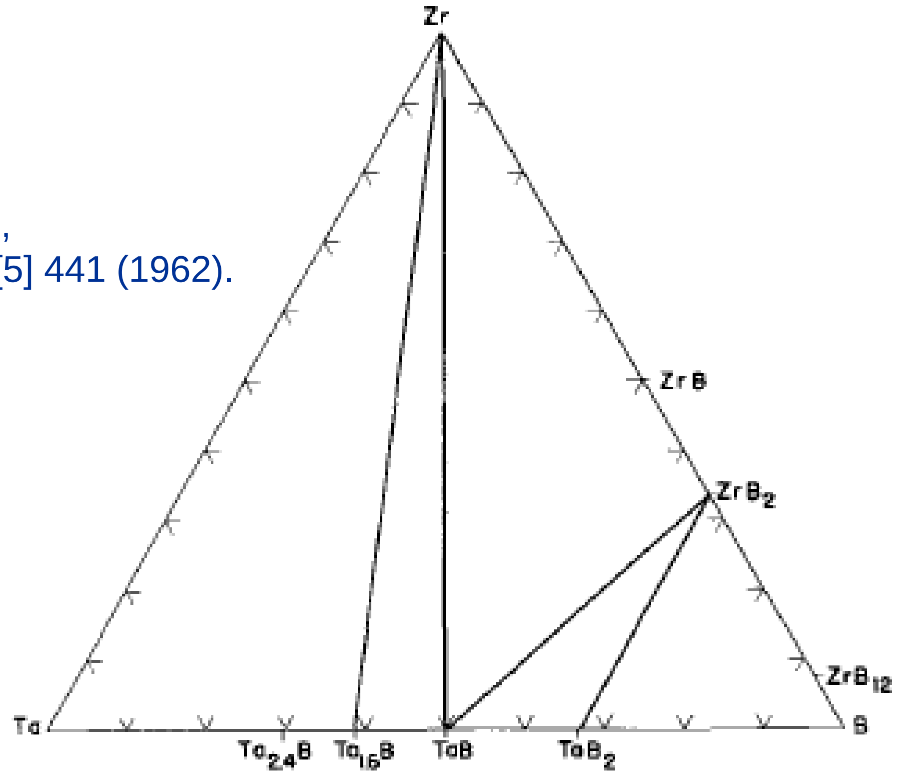


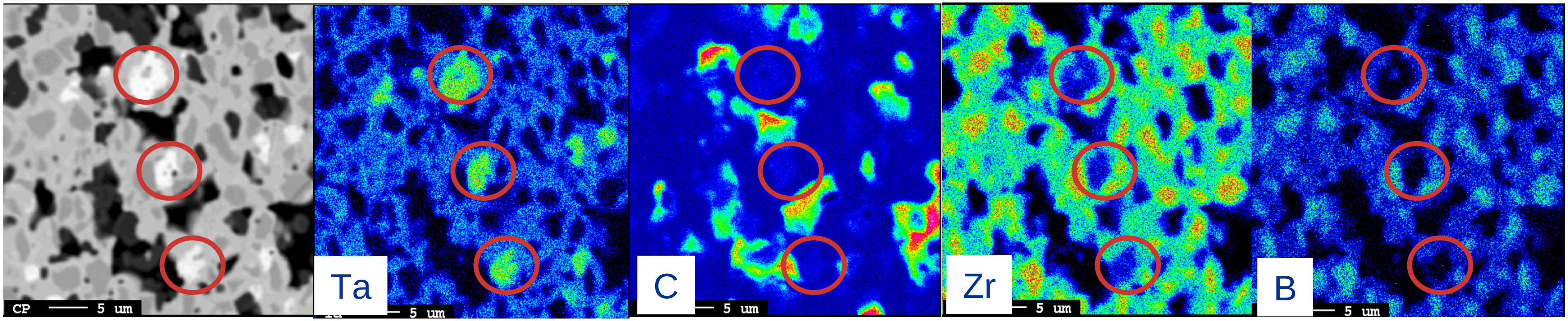
Fig. 1. Schematic phase diagram for the Ta-Zr-B system for a temperature of 1500°C.

Characterization of ZS20TS after 1927°C oxidation

- Extensive melt formation
- Characterizing phase formation after cooling
- Not necessarily equilibrium phase formation

Characterization of ZSTS(20) after oxidation at 1927°C: matrix phases

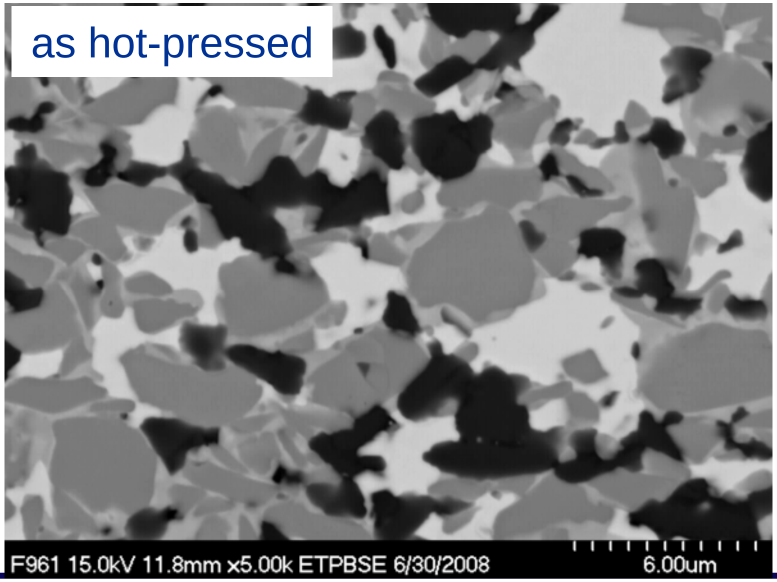
- $TaSi_2$ is gone. T_m $TaSi_2$ = 2200°C (HSC, Kosolapova)
- Four phases observed:
  - Phase 1: ZrB_2 B/Zr = 1.98
  - Phase 2: SiC C/Si = 1.05
  - Phase 3: $(Zr,Ta)B_x$ Zr/Ta = 3.47 B/(Zr+Ta) = 1.43
  - Phase 4: $(Zr,Ta)C_x$ Zr/Ta = 0.56 C/(Zr+Ta) = 1.42

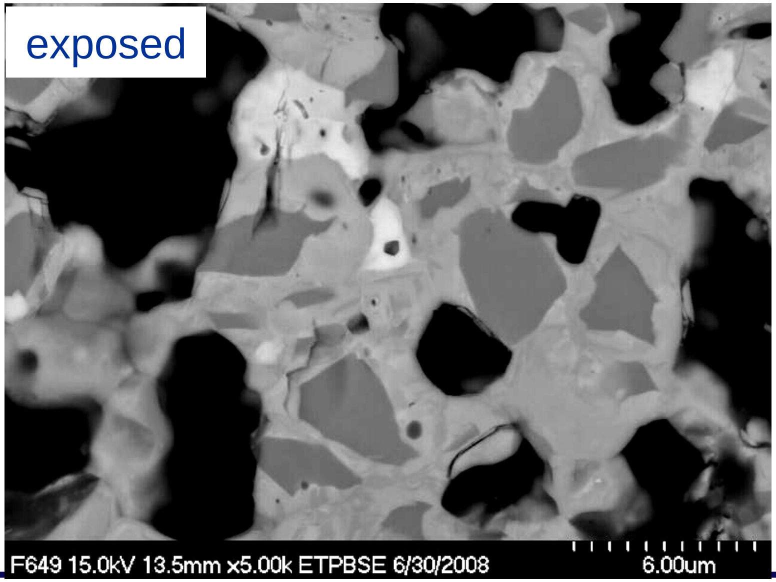


Ta-rich some C some Zr no B

Evolution of matrix after oxidation

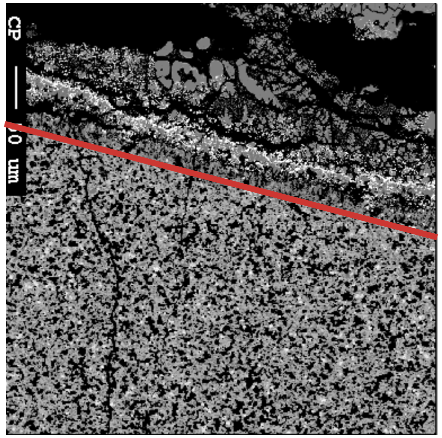
- Loss of $TaSi_2$, appearance of TaC
  - Active oxidation of $TaSi_2$ leaving Ta?
  - TaC more stable than SiC
  - $TaSi_2 + SiC + 1.5\ O_2(g) = TaC + SiO(g)$ ΔG_{rxn}=-79kJ/mol
- Change in phase distribution
  - Decrease of ZrB_2, SiC
  - (Increase of Zr,Ta)B_x

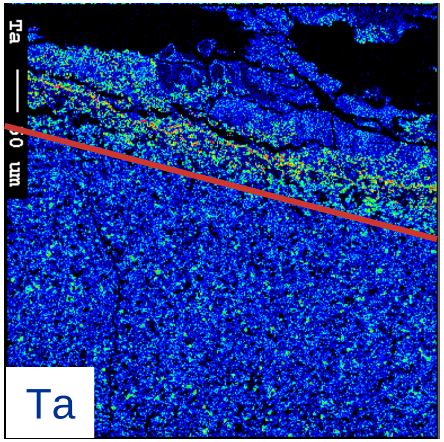


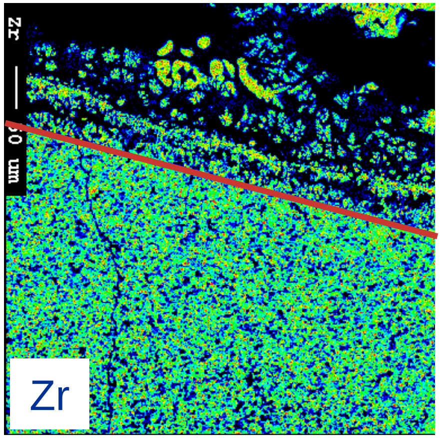


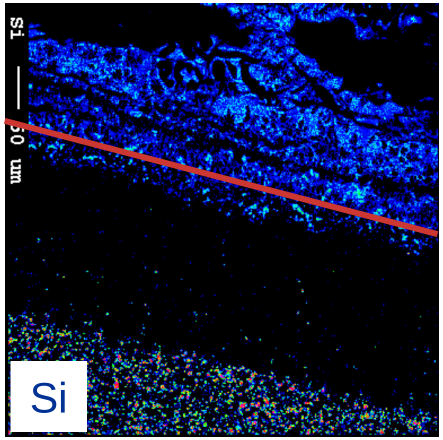
General characteristics of oxide layers

ZS20TS 1927°C 50 minutes air







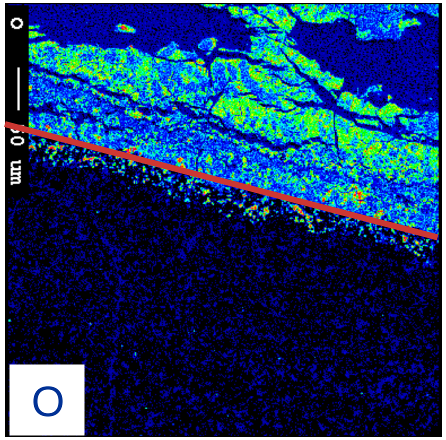


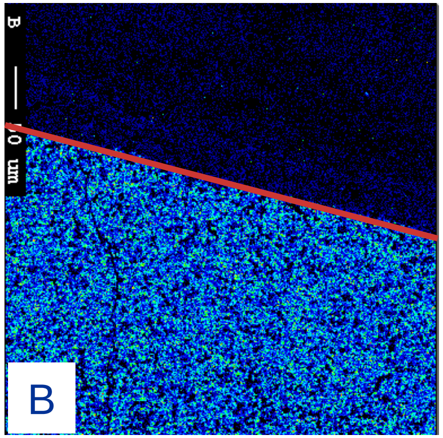
Ta concentrated near initial interface, but present throughout scale

Zr forms discrete oxide particles

Silica is present in most of scale, Si depletion layer below oxide

Oxides found below interface, silica?





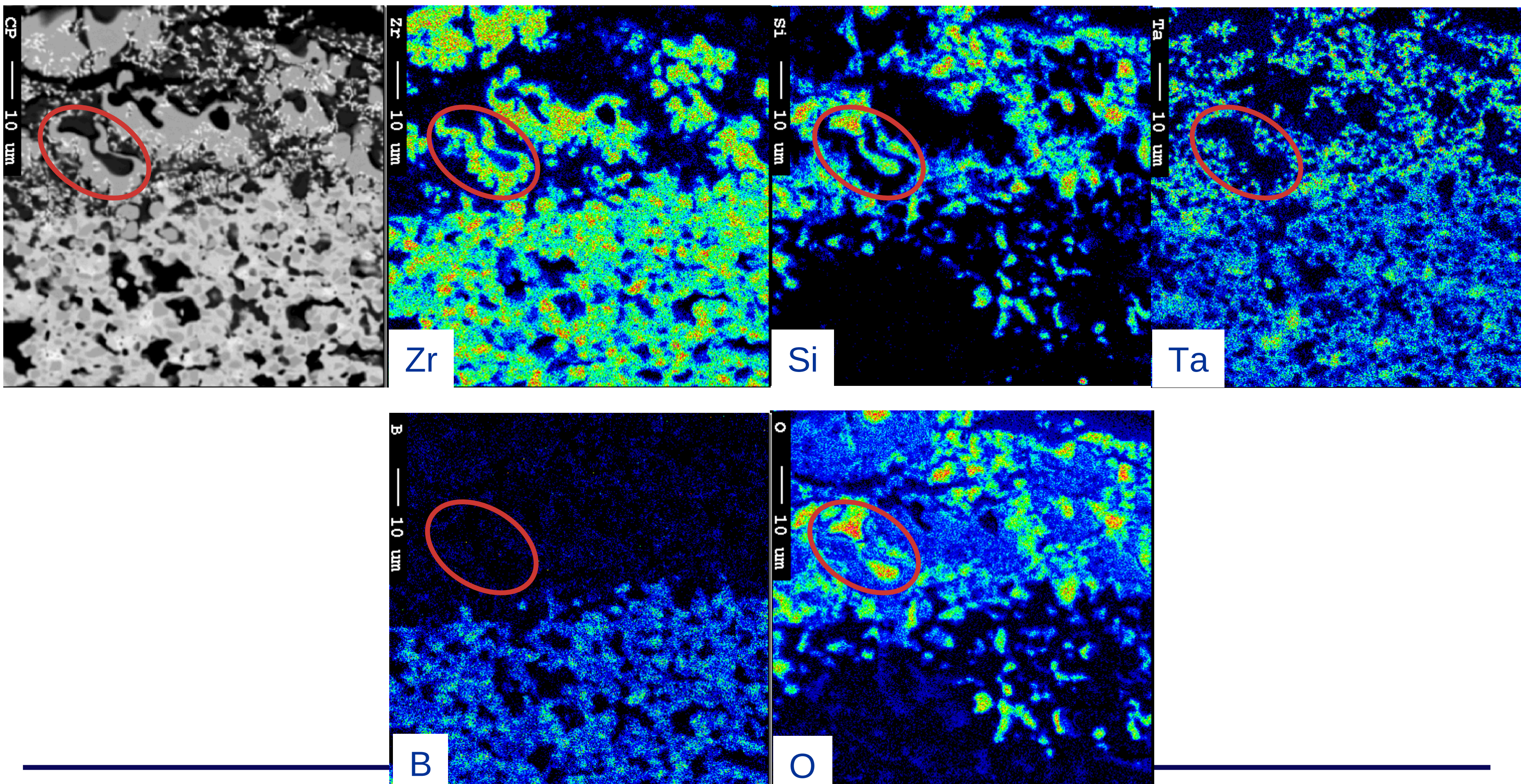
ZrB_2 and SiO_2 coexist in layer below interface. Some B in near surface oxide layer?

Characterization of ZS20TS after oxidation at 1927°C: oxide phases adjacent to matrix

ZrO_2 O/Zr = 1.96

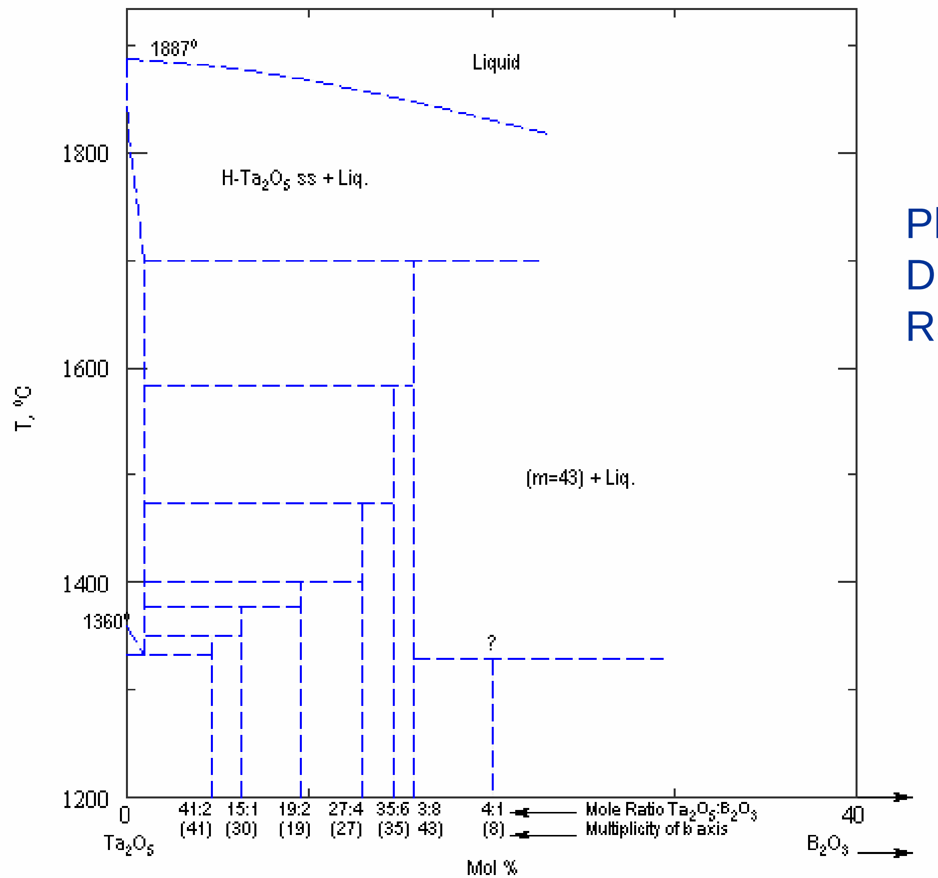
SiO_2 O/Si = 1.96

Ta(Zr)B(O) Ta/Zr = 7.49 B/O = 2.16 (B+O)/(Ta+Zr) = 1.36, not Ta_2O_5



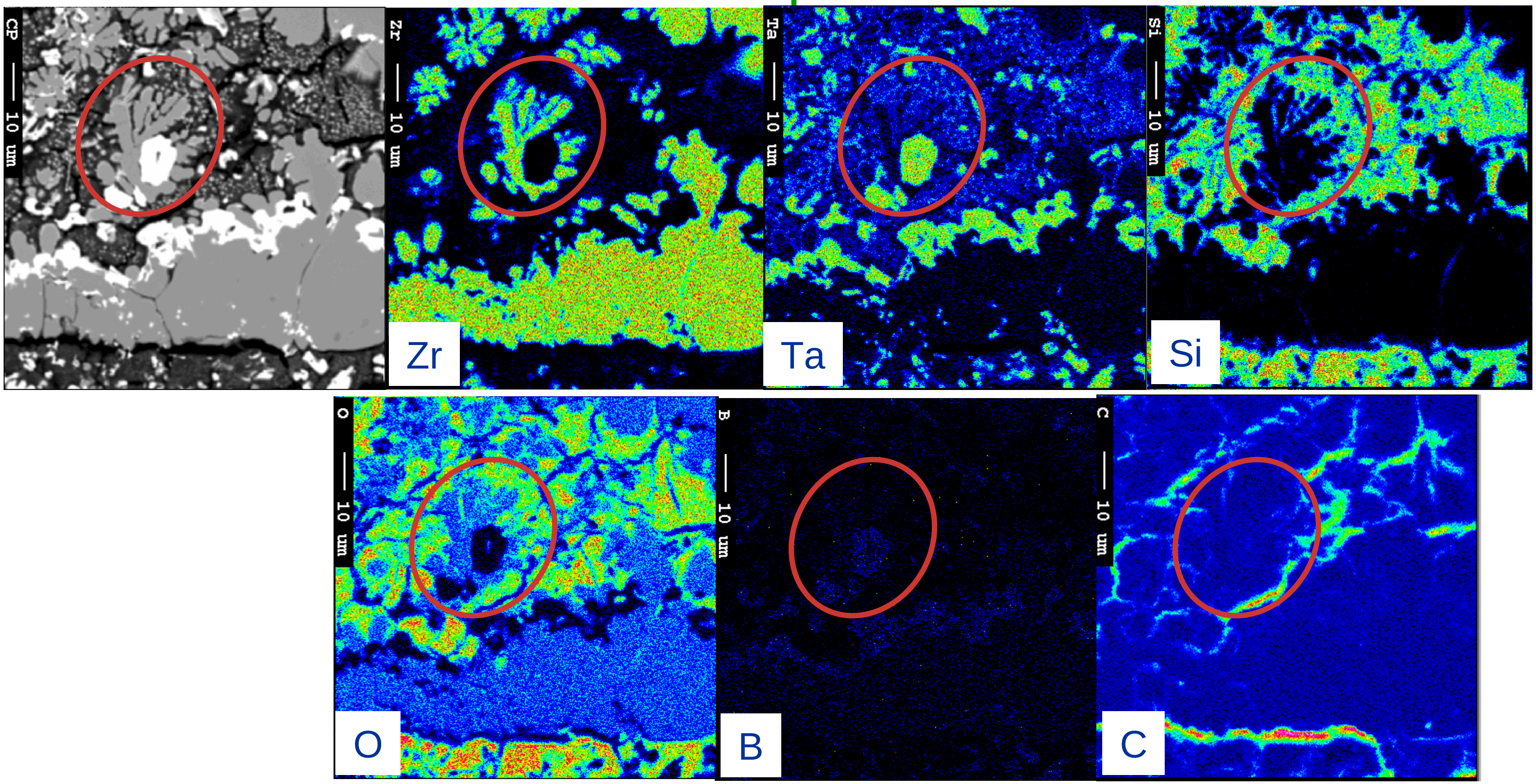
(Ta,Zr)(B,O)?

- TaB_2 sampling ZrO_2 underneath small Ta-rich particles?
- Ta oxyboride?
  - Oxynitrides and oxycarbides known to exist
  - Ta O B phase diagram



Phase Diagrams for Ceramists
Diagram 4392
RS Roth, JL Waring, 1970.

Characterization of ZS20TS after oxidation at 1927°C: middle portion of scale



ZrO_2 large continuous regions O/Zr = 1.98

SiO_2 O/Si = 2.39? some Ta 1.6at%

Ta(B,O) B/O = 1.71 (O+B)/Ta = 0.73 phase separated in silica

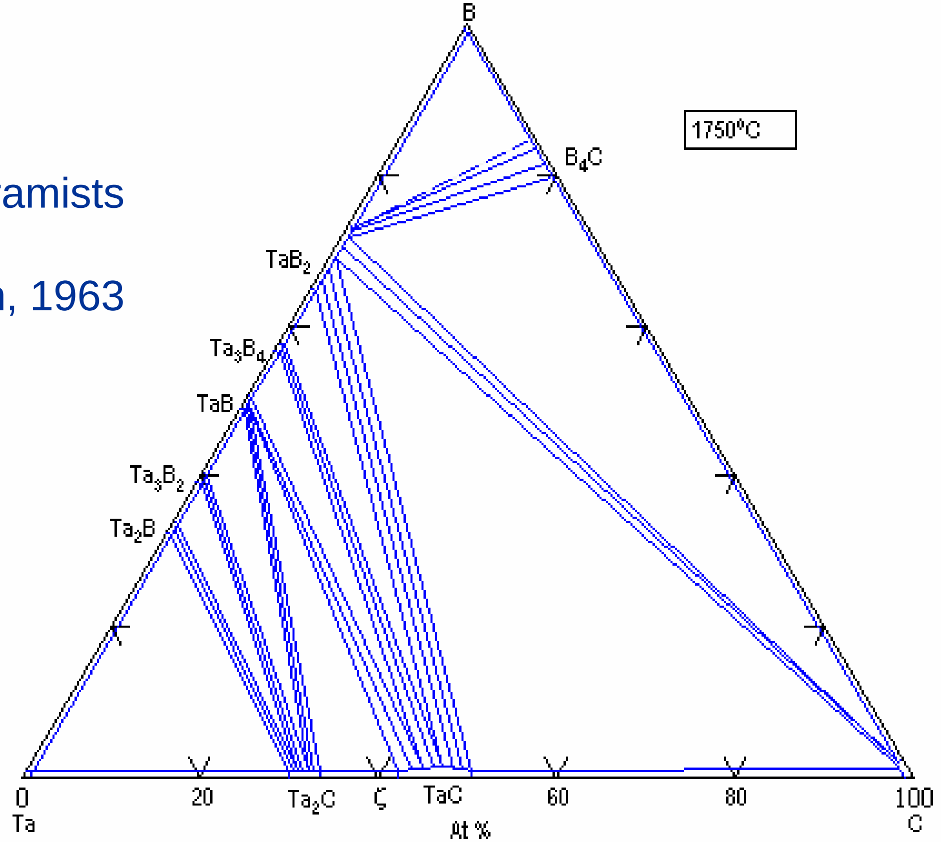
Ta(C,B) not expected: C/B = 1.34 (C+B+O)/Ta = 1.00

Additional phase not analyzed by microprobe

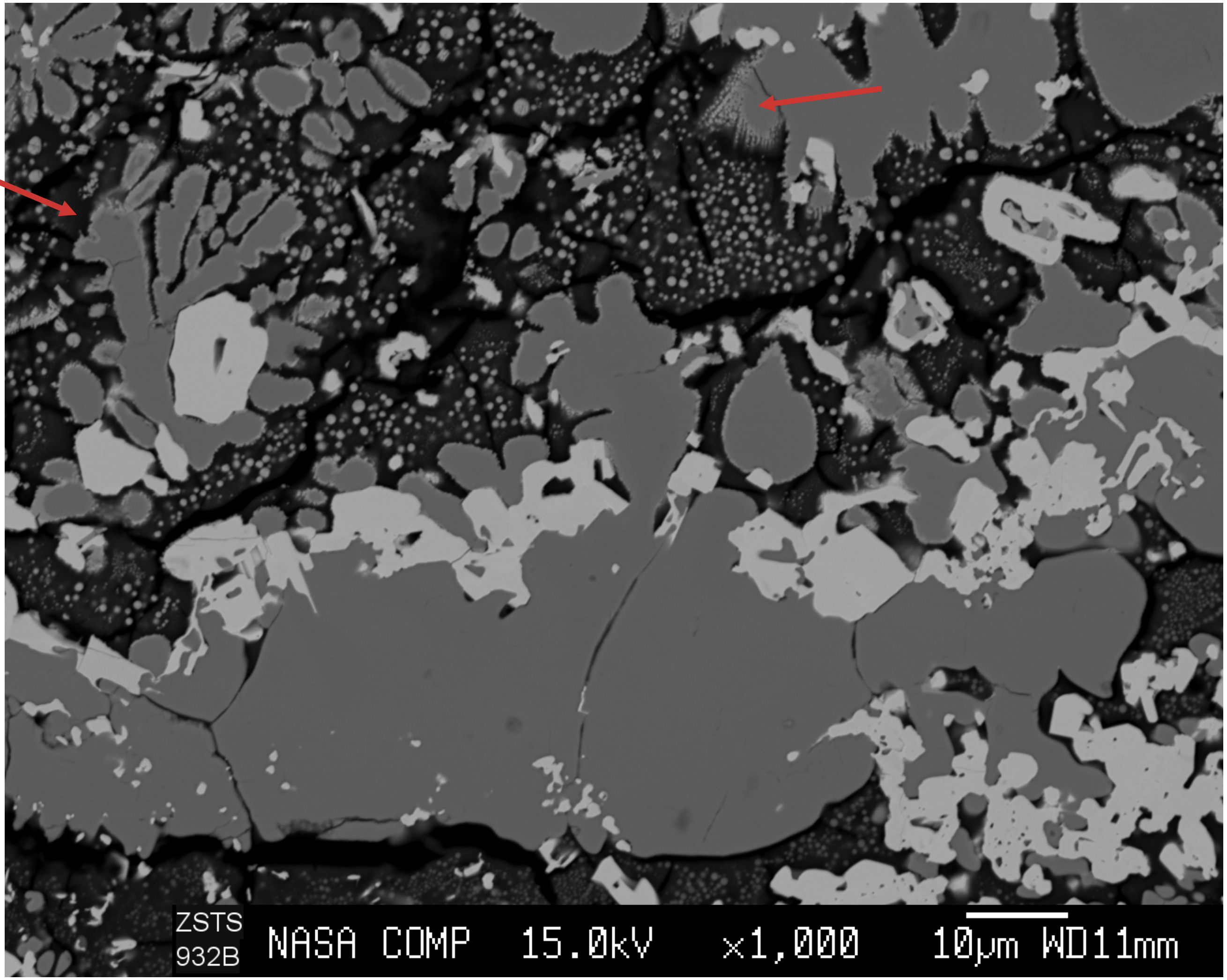
Ta(C,B)?

- TaC and TaB_2 both significantly less stable than oxide phase
  - ZrO_2 more stable than Ta_2O_5 (Ellingham diagram)
- Unexpected phase formation: TaC cubic, TaB_2 hexagonal
  - Artifact of sampling volume?

Phase Diagrams for Ceramists
Diagram 8865
Rudy, Benesovsky, Toth, 1963



TaZrO phase morphology on ZrO_2 suggests surface reaction, Phase V?



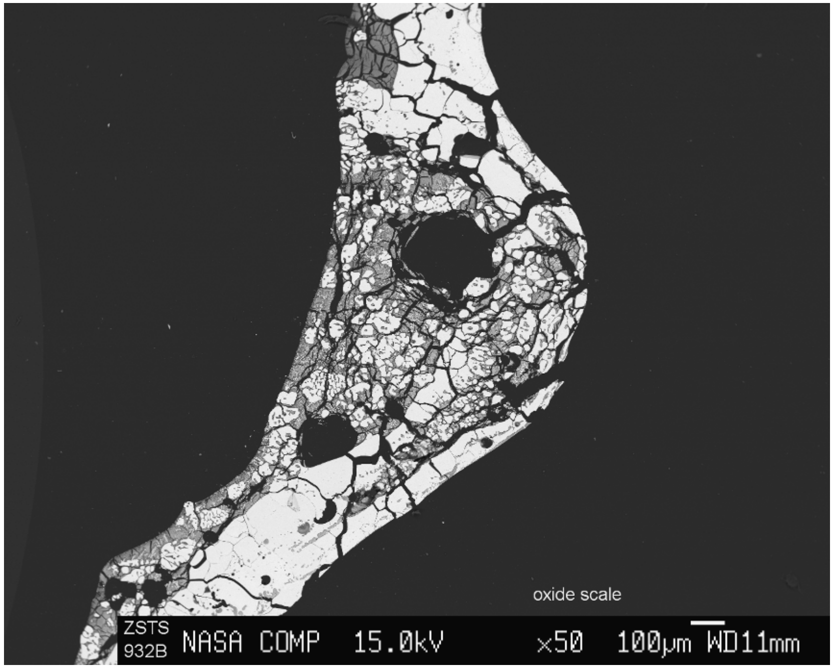
Characterization of ZSTS(20) after oxidation at 1927°C: loose outer portion of scale

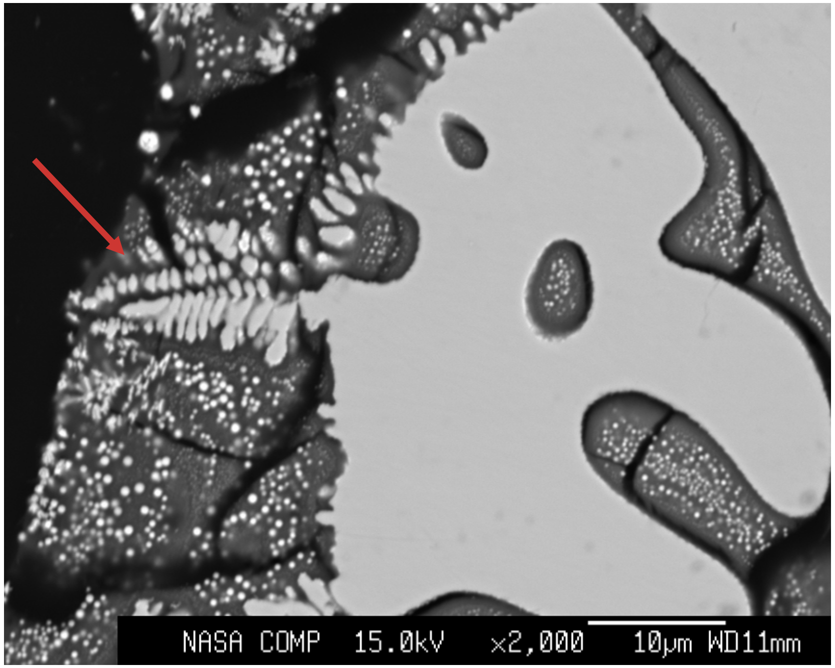
ZrO_2 O/Zr = 2.07 dendrites observed

SiO_2(Ta) O/(Si+Ta) = 2.917

(Zr,Ta)O phase separated in silica

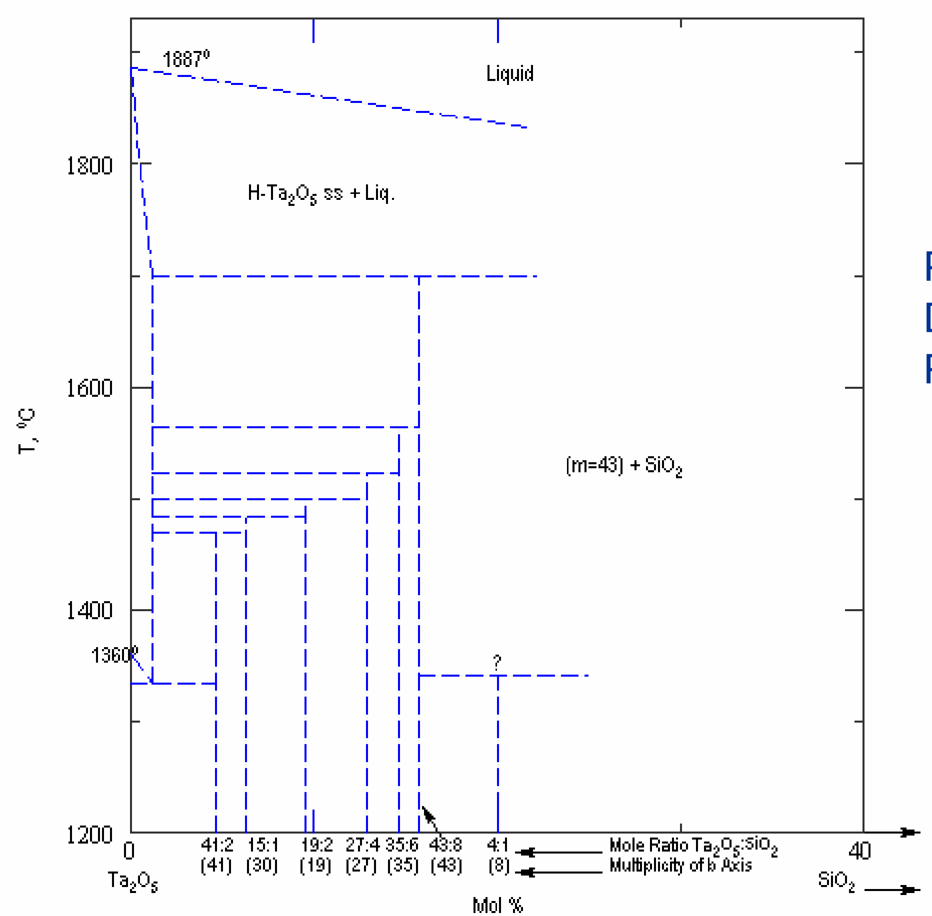
- Zr/Ta = 1.92, not Phase V, Zr/Ta= 5.5 to 6
- O/(Zr+Ta) = 2.47, expected ratio for Ta_2O_5





Ta Si O

- WDS results suggest Ta-O in solution with SiO_2
- Available phase diagram suggests ordering is possible



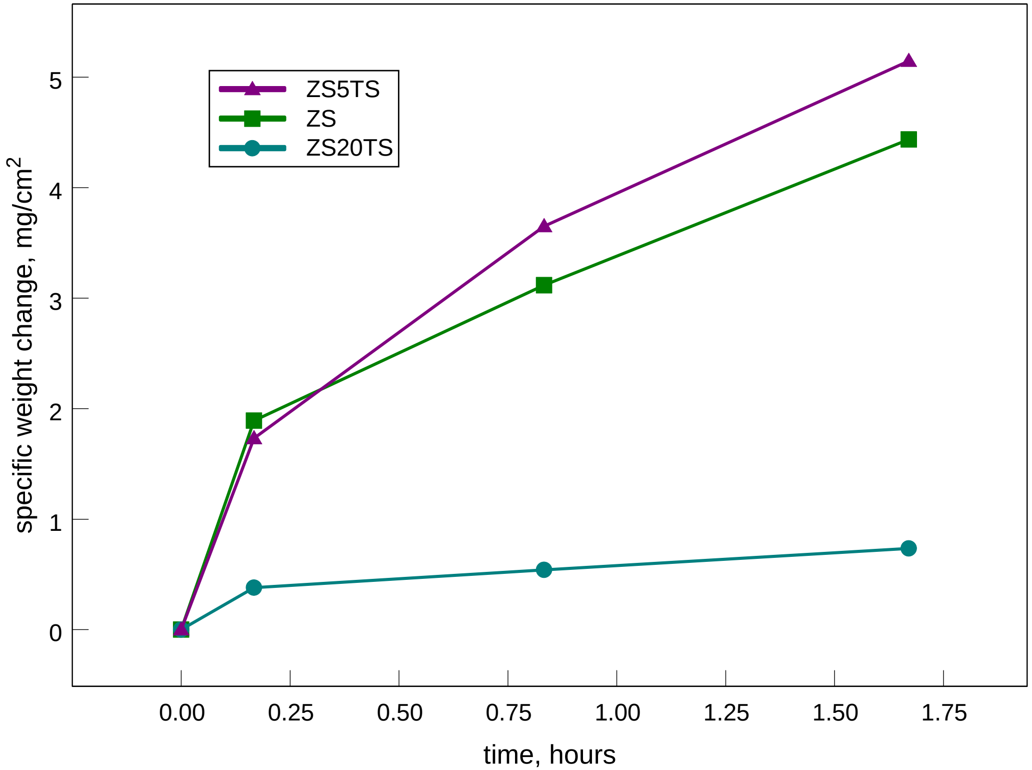
Phase Diagrams for Ceramists
Diagram 4448
RS Roth, JL Waring, 1970.

Summary of observations for ZSTS(20) oxidation at 1927C

- Zr- and Ta-borides form solid solution
- $TaSi_2$ is not stable after exposure at 1927°C, about 300°C<T_m
- Possible active oxidation of $TaSi_2$ resulting in SiO(g) and TaC formation
- Oxidation microstructure is fine near matrix interface, coarse at outer surface
- Ta(C,B) appears to remain unoxidized amidst ZrO_2 scale
- Unexpected formation of Ta(C,B) in scale?
- Melt formation: ZrO_2 SiO_2 Ta_2O_5 all in solution
  - Ta(B,O) phase separated in silica rich areas
  - Si(Ta)O
  - Dendritic structure of Phase V (?) on surface of ZrO_2, Ta(C,B)
  - Dendritic structure of ZrO_2 in outer scale

Optimization of $TaSi_2$ additions

Oxidation of ZS5TS at 1627°C in air



ZS20TS: 1, 5, and 10 cycles

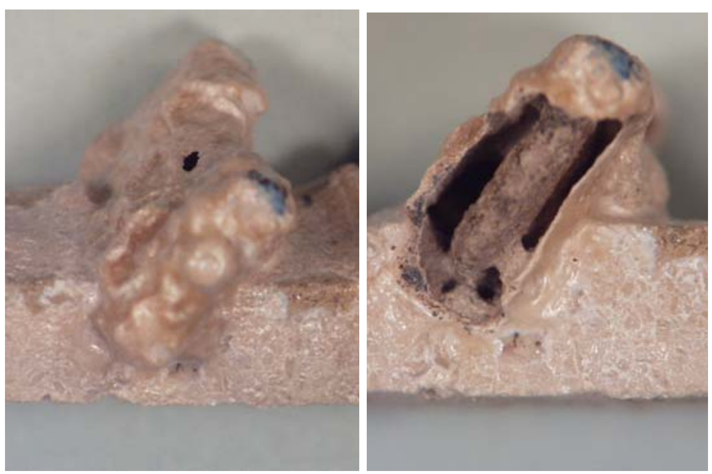
ZS5TS: 1, 5, and 10 cycles

ZS: 1, 5, and 10 cycles

Oxidation: 10 minute cycles at 1927°C in stagnant air

ZS5TS: 1, 5, and 7 cycles

ZS20TS: 1 cycle



ZS20TS: 5 cycles

ZS: 1, 5, and 10 cycles

Summary of oxidation results for ZS5TS

- 5 volume % addition of $TaSi_2$ to ZS is not enough to promote improved oxidation behavior at 1627°C
  - Oxidation weight gain and appearance similar to ZS (no $TaSi_2$ additions)

- 5 volume % addition of $TaSi_2$ to ZS still results in extensive melt formation and undesirable scale morphology during oxidation at 1927°C

- Oxidation behavior of ZS can not be improved at both 1627°C and 1927°C with $TaSi_2$ additions

Conclusions: ZrB_2-SiC-$TaSi_2$

- 20 v%$TaSi_2$ additions to ZrB_2 - SiC result in formation of phase separated glass and improved oxidation resistance at 1627°C
- At 1927°C excessive melt formation prevents dimensional stability of oxides formed from ZrB_2 - SiC -$TaSi_2$
- $TaSi_2$ reacts to form (Zr,Ta)B_x, Ta(C,B) as well as melt solution phases containing Ta, Zr, Si, O, B
- $TaSi_2$ additions can not be optimized to form both phase separated glass at 1627°C and oxides with dimensional stability at 1927°C.
- More phase stability work needed in UHTC systems

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