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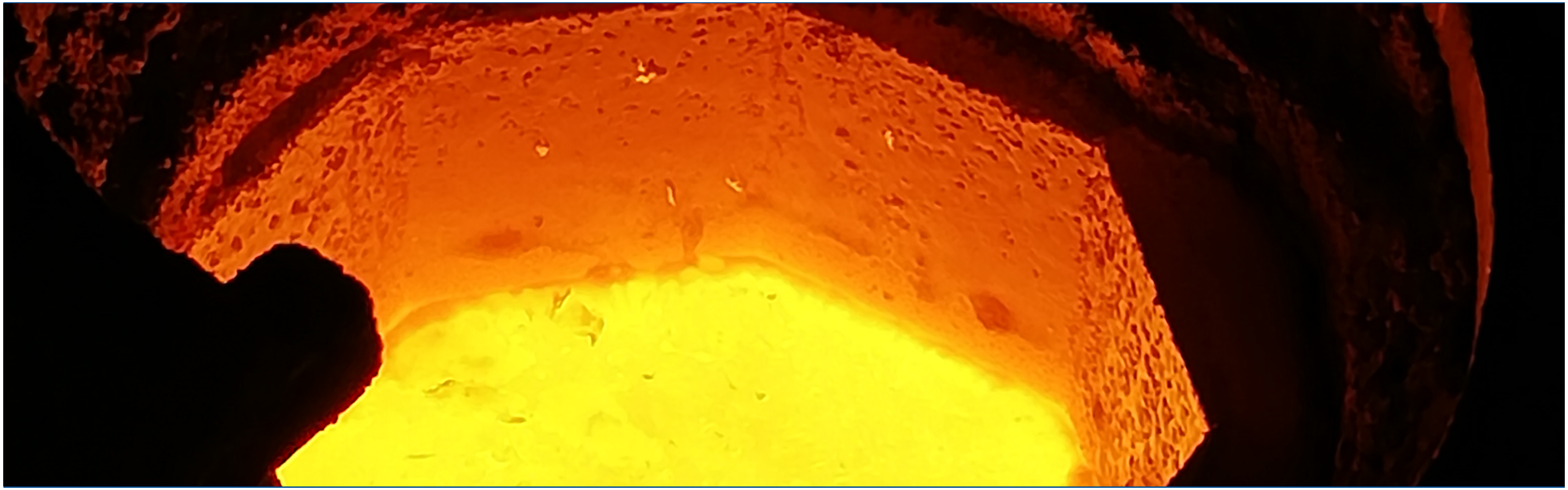

CORROSIVE INTERACTIONS OF GRAPHITE-BEARING SiC-CRUCIBLES DURING COPPER PROCESSING

Denise Ramler – 11th Freiberg Refractory Forum – 09.12.2020

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Outline

Introduction

- Process: Copper melting and alloying
- Refractory material: C-bonded SiC crucibles
- Problem: limited service life due to corrosion of the refractory material
- Solution: Improving corrosion resistance of the refractory material

→ **Understanding corrosion mechanisms is necessary for improving corrosion resistance**

Tab. 1: All tested refractory crucibles with different shaping methods, bonding agents and varying SiO_2/Al_2O_3 ratios

Material	Shaping method	Bonding agent	SiO_2/Al_2O_3 Ratio
T1	Roller-formed	pitch	1,7
T2	Isostatically pressed	pitch	3,3
T3	Roller-formed	resin	1,0
T4	Isostatically pressed	resin	2,0

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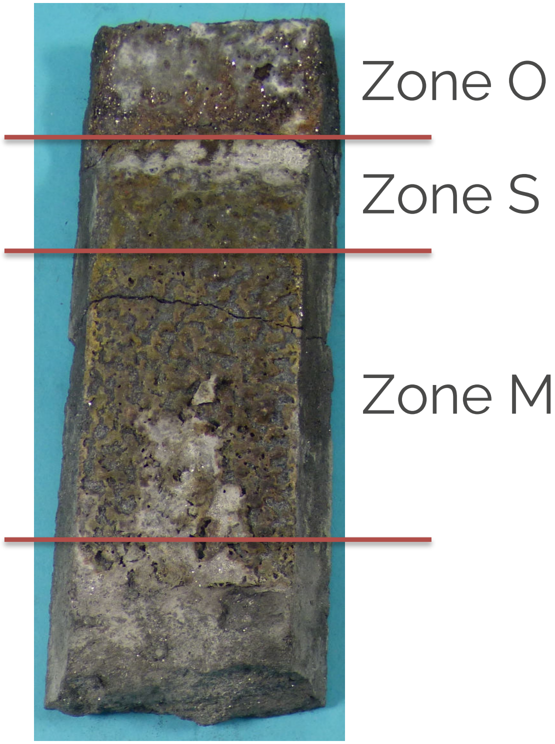
Experimental

- Induction Furnace Test at T = 1400° C
  - Testing of all 4 materials simultaneously
  - Impact of atmosphere, slag and Cu-Al alloy on refractory
  - 12h for fluoridic slag
  - Measuring erosion and infiltration depth
- SEM + EDX analysis before and after testing
- X-Ray Diffraction before and after testing
- Thermodynamic calculations via FactSage

Fig. 1: Induction Furnace Test Setup

Results

T3 before testing



After test with fluoridic slag

Results

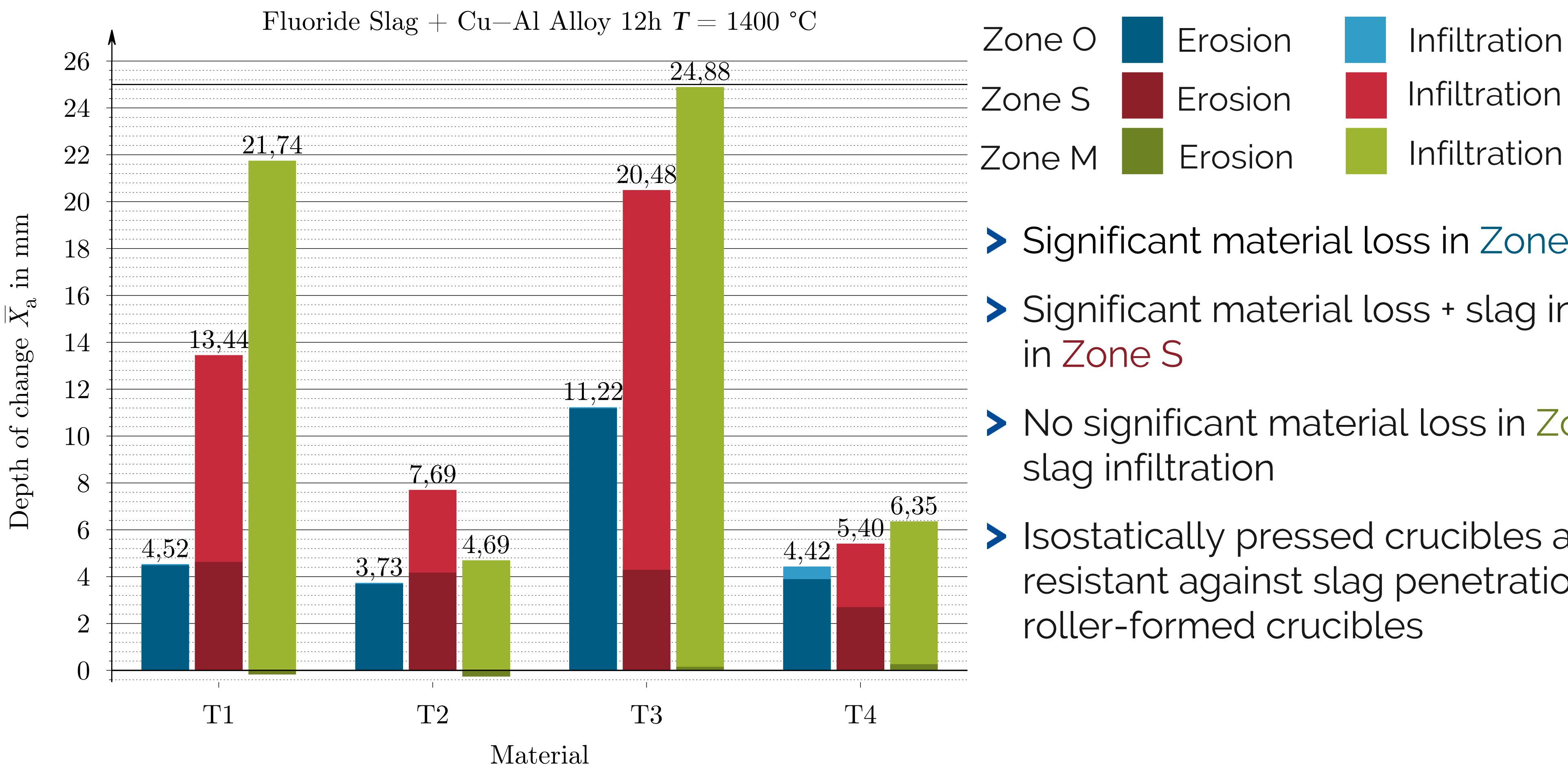


Fig. 2: Depth of change in mm. Consists of depth of erosion + slag infiltration.

- Significant material loss in Zone O
- Significant material loss + slag infiltration in Zone S
- No significant material loss in Zone M but slag infiltration
- Isostatically pressed crucibles are more resistant against slag penetration than roller-formed crucibles

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Results for Zone O

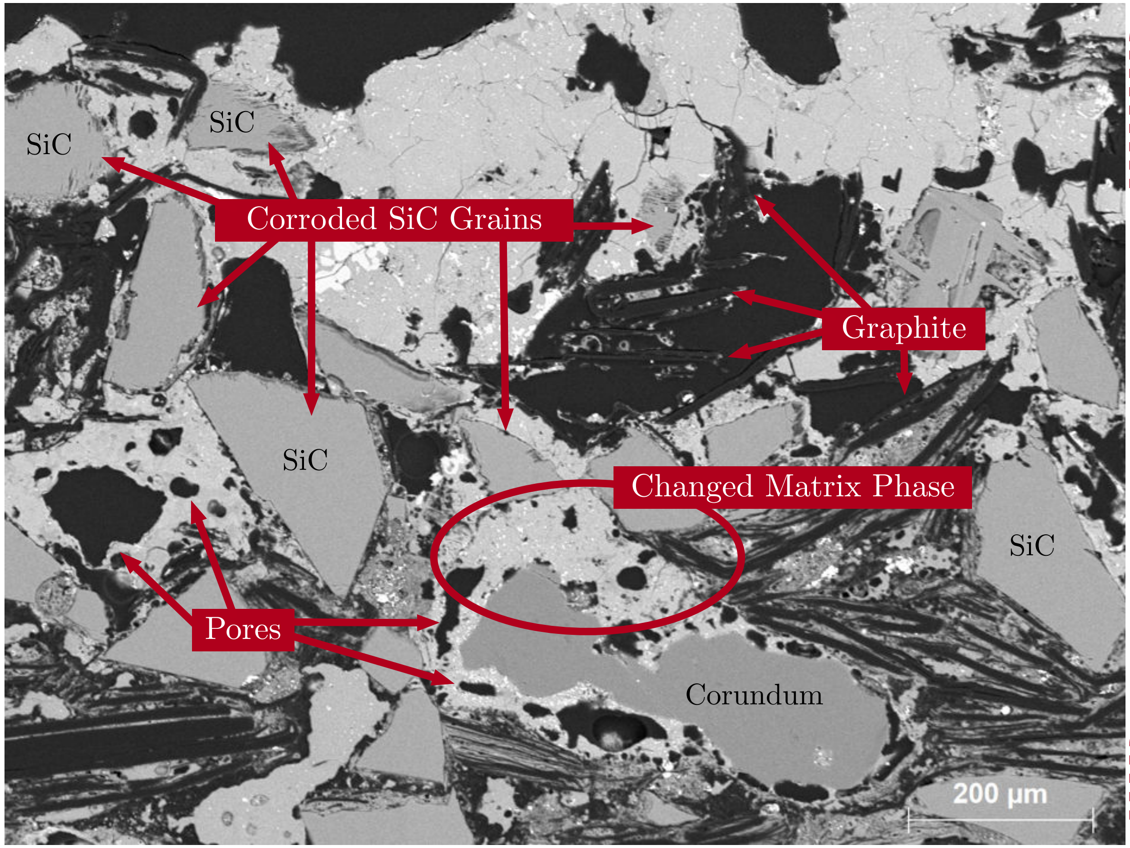


Fig. 3: 25 kV, BSE, 100x SEM image of T3 in Zone O after IF-Test with fluoridic slag.

$$2\,\mathbf{C(s)} + O_2(g) \longrightarrow 2\,CO(g)$$

$$\mathbf{SiC(s)} + O_2(g) \longrightarrow SiO(g) + CO(g)$$

$$\mathbf{SiC(s)} + {}^3/_2\,O_2(g) \longrightarrow SiO_2(s) + CO(g)$$

$$\mathbf{Al_2O_3(s)} + 6\,KF(g) \longrightarrow 2\,AlF_3(s,l) + 3\,K_2O(g)$$

$$\mathbf{Al_2O_3(s)} + 8\,KF(g) \longrightarrow 2\,KAlF_4(g) + 3\,K_2O(g)$$

$$2\,KAlF_4(g) + 2\,\mathbf{SiO_2(s)} \longrightarrow 2\,SiF_4(g) + K_2Al_2O_4(l)$$

$$3\,\mathbf{SiC(s)} + 4\,AlF_3(s,l) \longrightarrow 3\,SiF_4(g) + Al_4C_3(s)$$

$$2\,K_2O(s) \longrightarrow 4\,K(g) + O_2(g) \qquad T = 623{,}15\ K$$

Results for Zone S

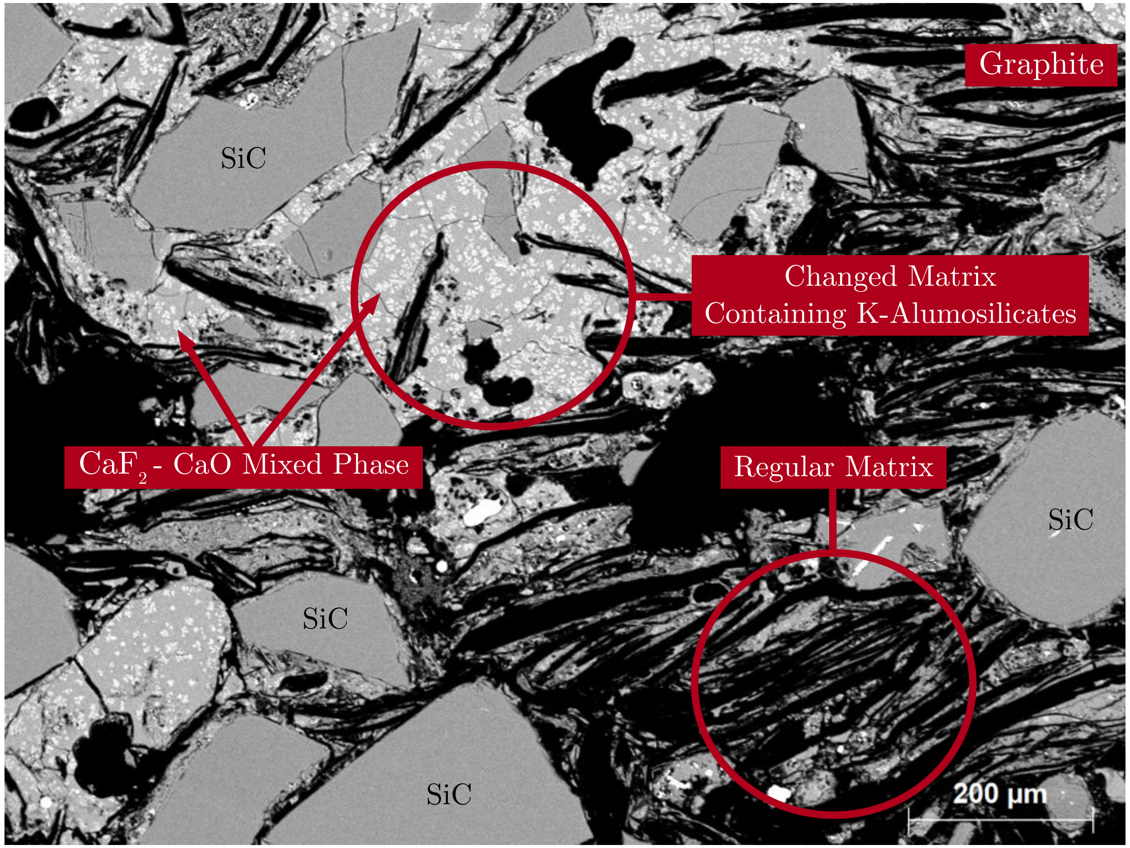


Fig. 4: 25 kV, BSE, 100x SEM image of T3 in Zone S after IF-Test with fluoridic slag.

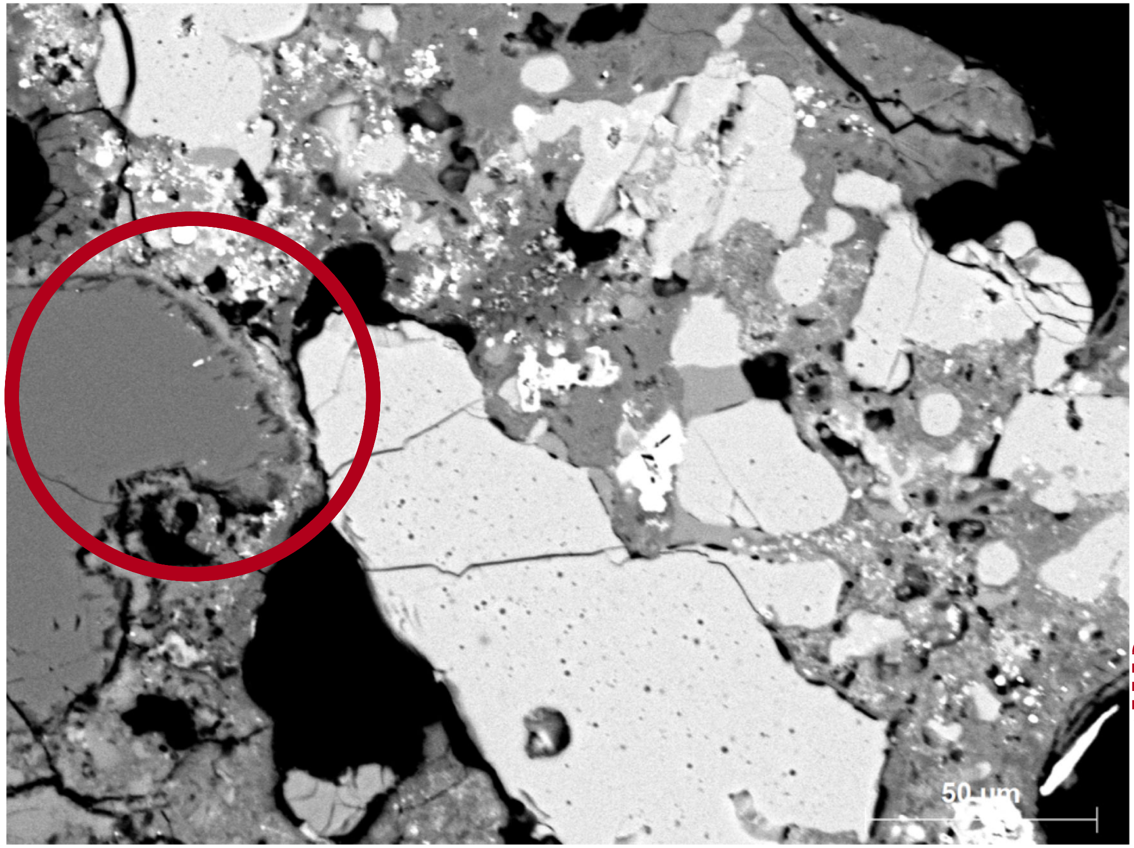
$\mathbf{SiO_2(s)} + 2\,CaF_2(l) \longrightarrow 2\,SiF_4(g) + 2\,CaO(s)$

$2\,K_3AlF_6(l) + 3\,\mathbf{SiO_2(s)} \longrightarrow 3\,SiF_4(g) + 2KAlO_2(l) + 2\,K_2O(g)$

$2\,K_2O(s) \longrightarrow 4\,K(g) + O_2(g)$ $T = 623{,}15$ K

$2\,\mathbf{C(s)} + O_2(g) \longrightarrow 2\,CO(g)$

Results for Zone S



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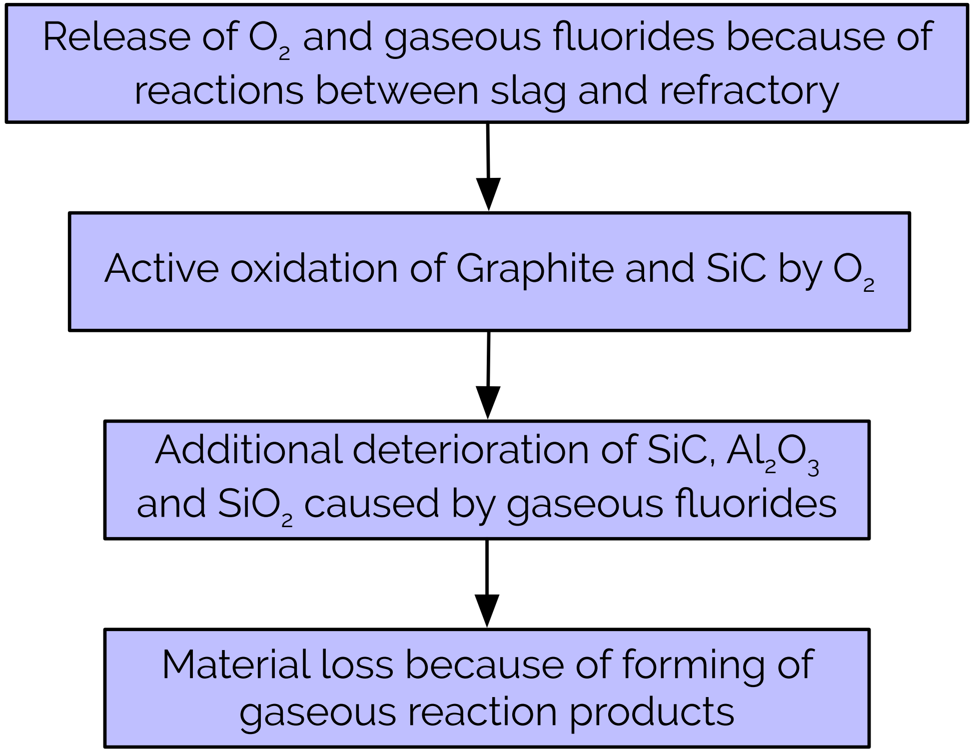
T = 623,15 K

$$2\,\mathbf{C(s)} + O_2(g) \longrightarrow 2\,CO(g)$$

$$\mathbf{SiC(s)} + O_2(g) \longrightarrow SiO(g) + CO(g)$$

Conclusion

Corrosion mechanism for Zone O

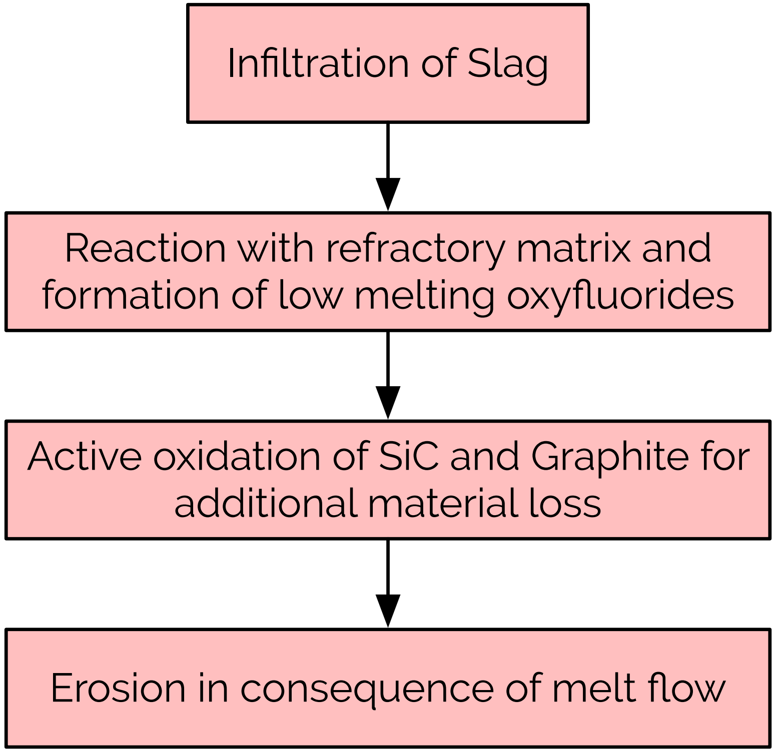


- Mainly by dissociation of previously formed K_2O
- Rapid reaction and no passivation of SiC to SiO_2
- High alumina content problematic: Formation of gaseous aluminofluorides

  → easily transported through the material for further corrosive attack on SiO_2 and SiC

Conclusion

Corrosion mechanism for Zone S



- Due to low viscosity of slag
- Low viscosity of oxyfluorides enables quick infiltration and transport of reactants

  → high alumina content lowers viscosity which promotes infiltration
- O_2 provided by previous reaction of slag with matrix to form oxyfluorides
- Easily eroded due to the low viscosity of the formed oxyfluoride phase within the crucibles

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Acknowledgements

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THANK YOU FOR YOUR INTEREST.