Single crystal and sintered alumina corrosion in liquid sodium

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SINGLE CRYSTAL AND SINTERED ALUMINA CORROSION IN LIQUID SODIUM

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Context and objectives

Ceramic materials for the core catcher:
Alumina is one of the candidate under studies for the 4th nuclear reactor programme (ASTRID) (Zirconia being the reference ceramic)

Apart from thermomechanical effects, the corrosion proceed by reaction with liquid sodium or its impurities (mainly oxygen), giving either homogeneous corrosion or localized corrosion if reactants are concentrated at the grain boundaries (GB).

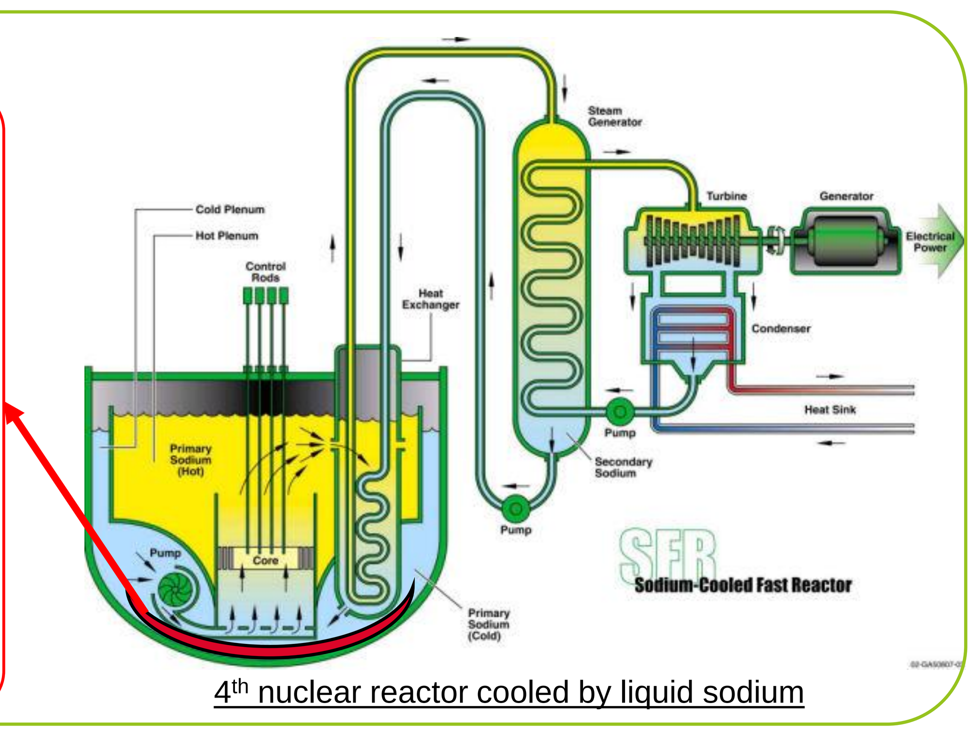
Silica traces segregated at the GBs are reported to enhance fast intergranular corrosion (IGC) in alumina that forbid the study of other corrosion phenomenon [Kano-95].

Any interactions between the liquid metal and the structural materials must be well understood and predicted to guarantee a 60 years service life-time as well as resistance to incidental conditions.

Compare polycrystal to monocrystal to define IGC-free ceramic material, to identify corrosion phenomena and quantity first corrosion rates vs. T and [O]

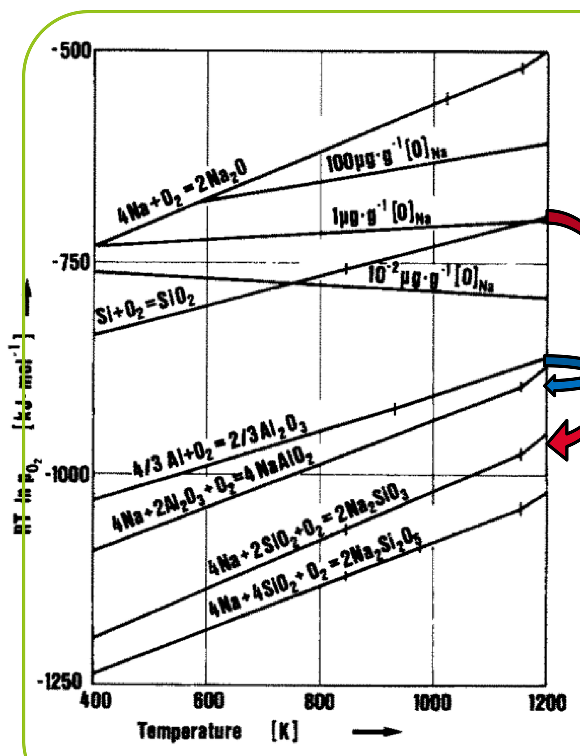
Core catcher : collect and allow cooling down all of melted reactor materials in case of reactor meltdown

Conditions: in contact with liquid sodium, 60 years, 400°C, [O]<~10 wt. ppm as potential casing of the ceramic material cannot be inspected nor repaired



4th nuclear reactor cooled by liquid sodium

Thermochemistry



Ellingham diagram [Jung-83])

- Aluminate and silicate are more stables at any reactor operating conditions, meanings kinetics control is required
- Kinetics for silicates formation is reported as fast for T>~300°C [Jung-83]

$SiO_2+Na_2O = Na_2SiO_3$ -230 kJ/mol at 400°C
$3SiO_2+4Na = 2Na_2SiO_3 + Si$ -136 kJ/mol

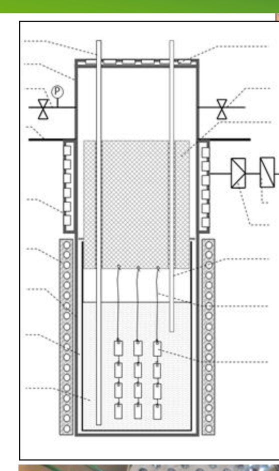
- Almost no data available for alumina, reaction not identified [Jung-83]

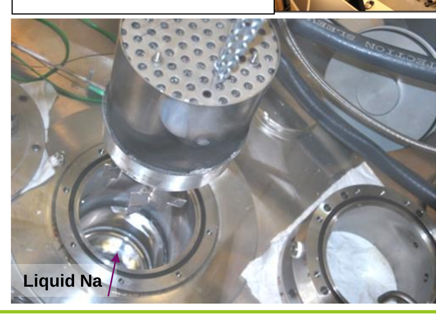
$2Al_2O_3 + 3Na = 3NaAlO_2 + Al$ -9 kJ/mol at 400°C
$Al_2O_3 + Na_2O = NaAlO_2$ -180 kJ/mol

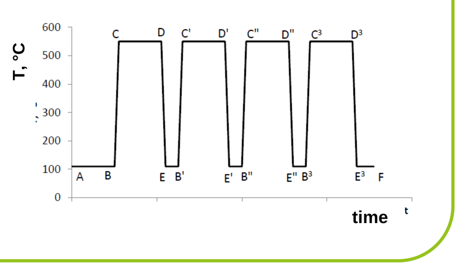
This study :
T & [O] effects on 'dissolution' of alumina and IGC

Experimental

- **Static liquid sodium** (2.3 kg- Mo crucible)
- Sintered alumina : Degussit AL23 - 99.7% purity (60 ppm SiO_2), no open porosity, tube (OD4- ID2 mm) and Sapphire supplied by Rubis SA(D20 mm rod)
- **Sodium chemistry control**
  - Purification (hot trapping by Zr foil at 630°C – 75h: <0.1 wt. ppm to 1-5 ppm)
  - Decantation at low T (105°C – 100h : 40 ppm)
  - Oxygen addition (Na_2O): 200 ppm
- **Temperature: 450 °C & 550 °C**
- **Duration:** from **250 h** to **4600 h**



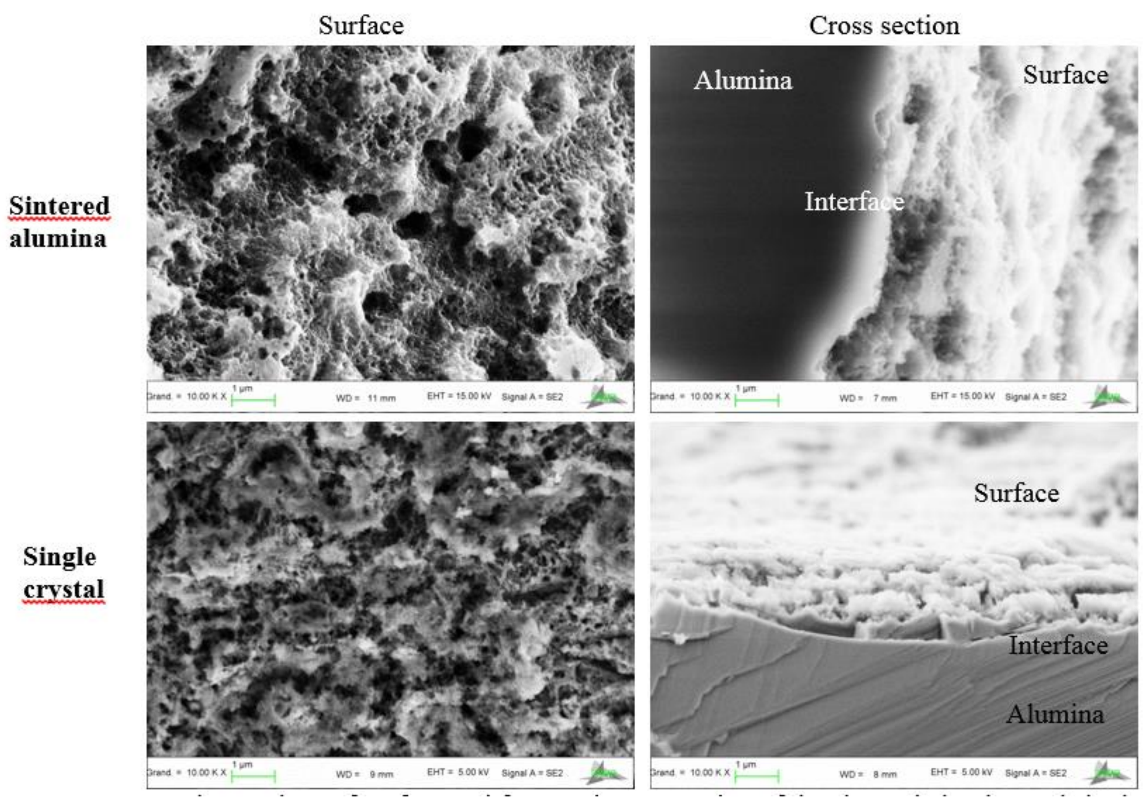




Morphologies

Surface and fractured cross section of sintered alumina & Sapphire

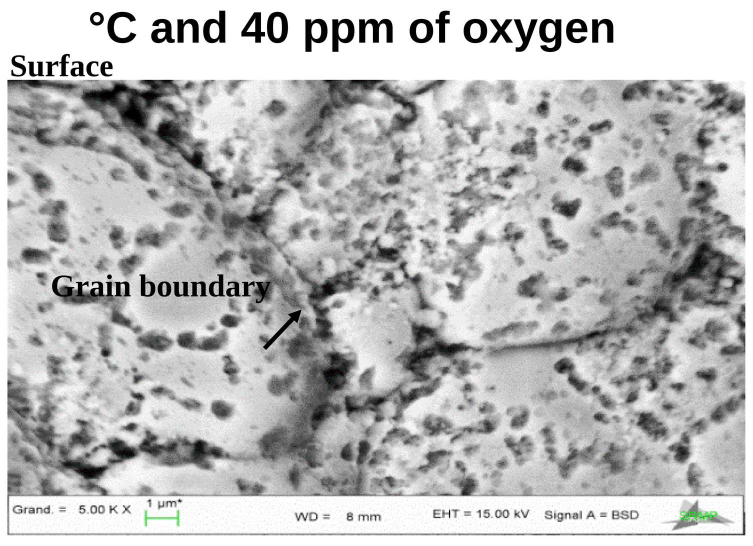
Exposure at 550 °C, 1-5 ppm of oxygen and 3000 h

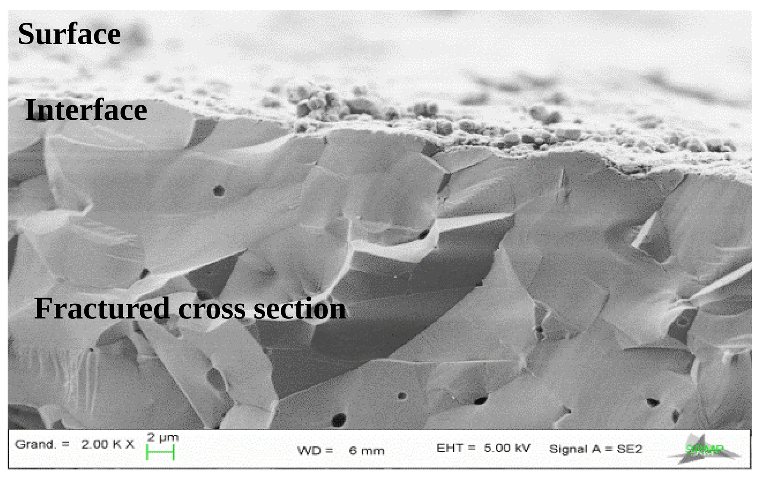


Fractured surfaces are trans-granular for all conditions up to the interface, demonstrating the absence of IGC

Pure and dense sintered alumina presents the same behavior as the single crystal to the condition that the grain boundary corrosion is negligible, which is the case for this high purity grade of sintered alumina

Sintered alumina after 1000h at 450 °C and 40 ppm of oxygen

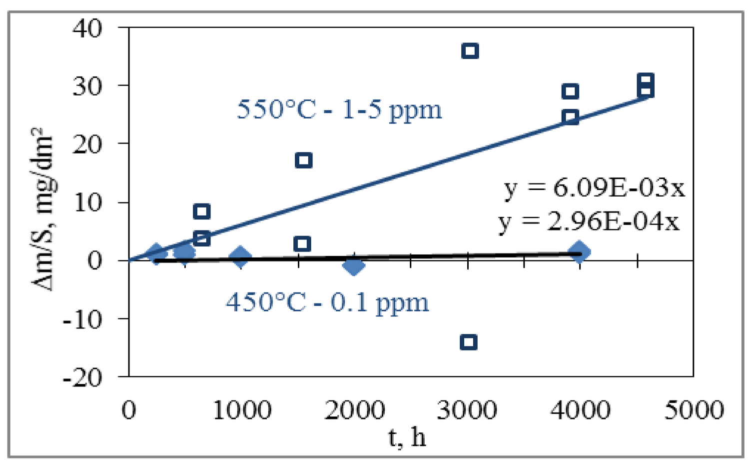




Porosity dimensions tend to increase with time and temperature (in relation with sodium residues after ethanol cleaning) eventually covering all of the surface

Corrosion rates

Weight loss of sintered alumina at 450°C and 550°C at low O



Supposing linear kinetics for low O content:
- 0.14 mg/dm²/d or 1.4 µm/y at 550 °C
- 0.007 mg/dm²/d or 0.07 µm/y at 450 °C

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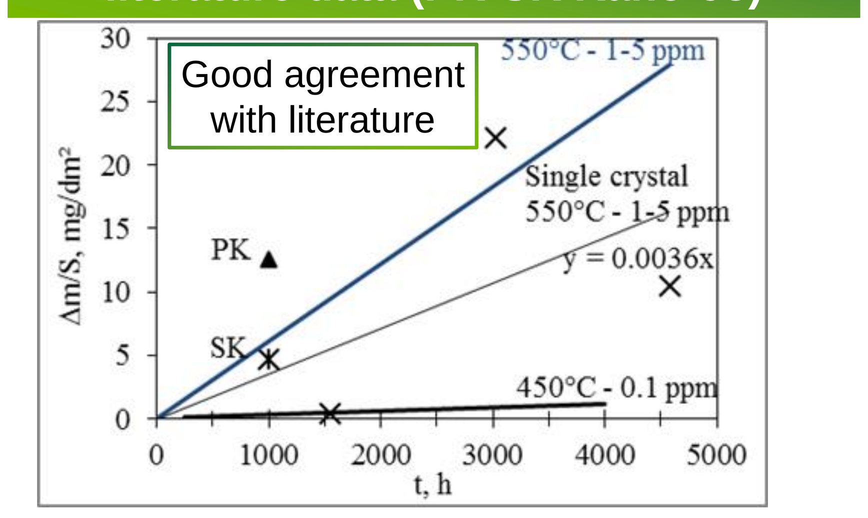
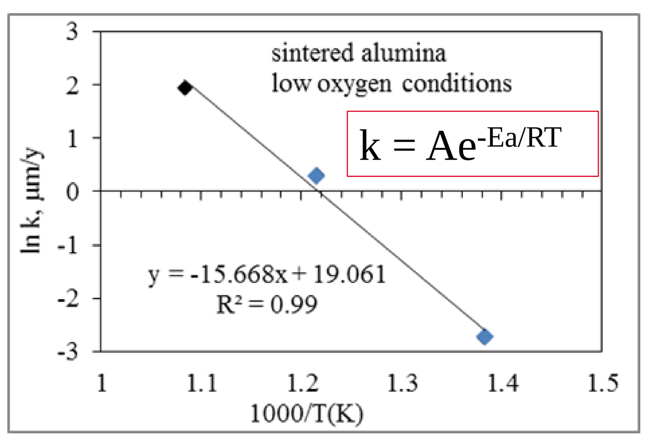
Single crystal weight loss at 550°C compared to sintered alumina and literature data (PK-SK Kano-95)



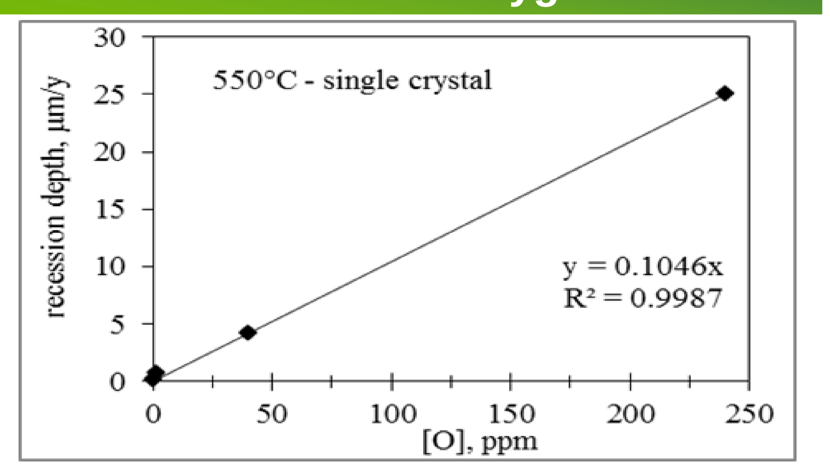
GB effect: dissolution rate twice greater for sintered alumina than for single crystal

Weight loss interpreted as equivalent to a dissolution with intermediate formation of $NaAlO_2$ that dissolves in Na or in water after sodium exposure

Arrhenius plot for sintered alumina at 450, 550 and 650 °C [Kano-95] in low oxygen content



Recession depth of single crystal at 550 °C as function of oxygen content



Dissolution rate: R=0.011.[O] (mg/dm²/d – ppm)

Temperature effect:
Apparent activation energy of 130 kJ/mol or 1.35 eV

Dissolved oxygen effect:
Straight dependence with oxygen content:
- Main reaction is $Al_2O_3+Na_2O(d)= NaAlO_2$
- First-order reaction kinetics with respect to oxygen content at the temperature of 550 °C

Conclusion and prospect

First step to a better understanding of the mechanisms of degradation and a guide for the elaboration or selection of ceramics that would be compatible with sodium on the long term:
1- High density, no open porosity and high purity required to avoid intergranular corrosion in liquid Na
2- Homogeneous corrosion of alumina equivalent to dissolution through a mechanism yet to elucidate
3- Corrosion rates of 0.07 to 0.14 µm/y assessed from weight losses measured at 450°C and 550°C in low oxygen conditions in agreement with the few available literature data
4- Apparent activation energy evaluated to 130 kJ/mol (1.35 eV) suggesting solid phase diffusion control as limiting step for the corrosion mechanism
5- First-order reaction kinetics with respect to dissolved oxygen at 550 °C
In prospect : confirm these results with additional tests, elucidation of the formation of sodium aluminate mechanism, hydrodynamics effect on corrosion rate, and extrapolation of these results to other ceramic materials such as zirconia.

Aknowledgements

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