Compatibility of alumina with eutectic Pb-Li alloy

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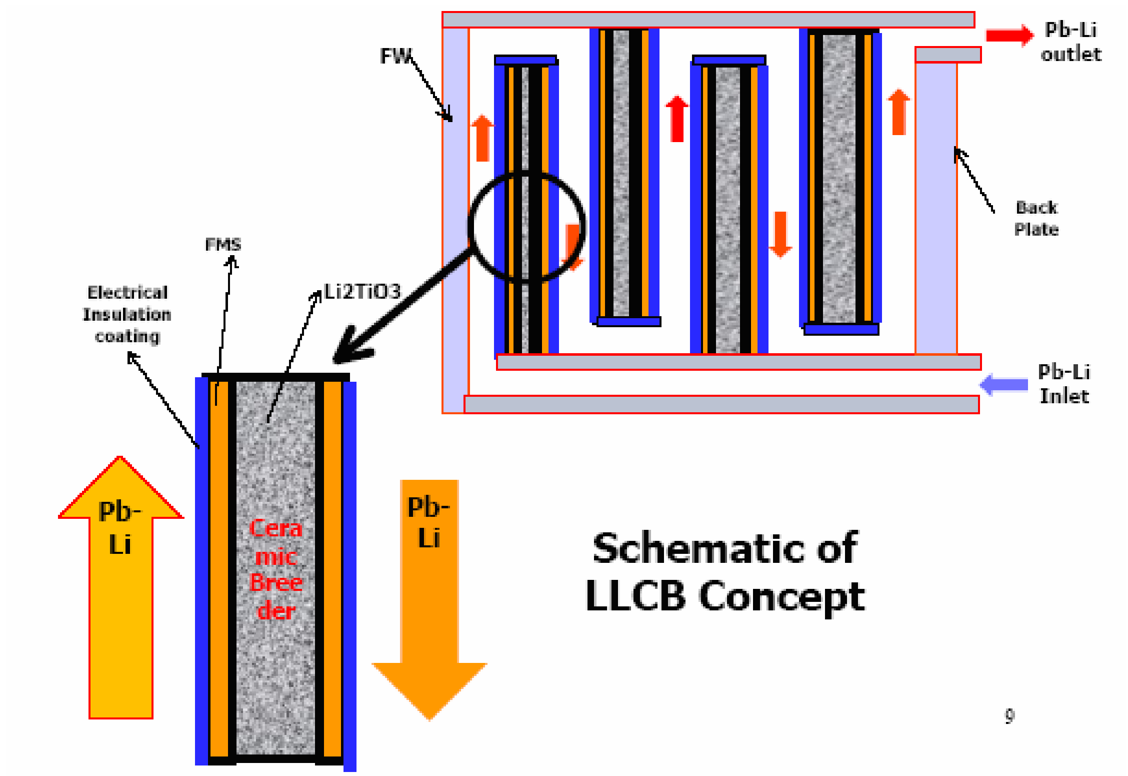
Bhabha Atomic Research Centre

Important Components in ITER

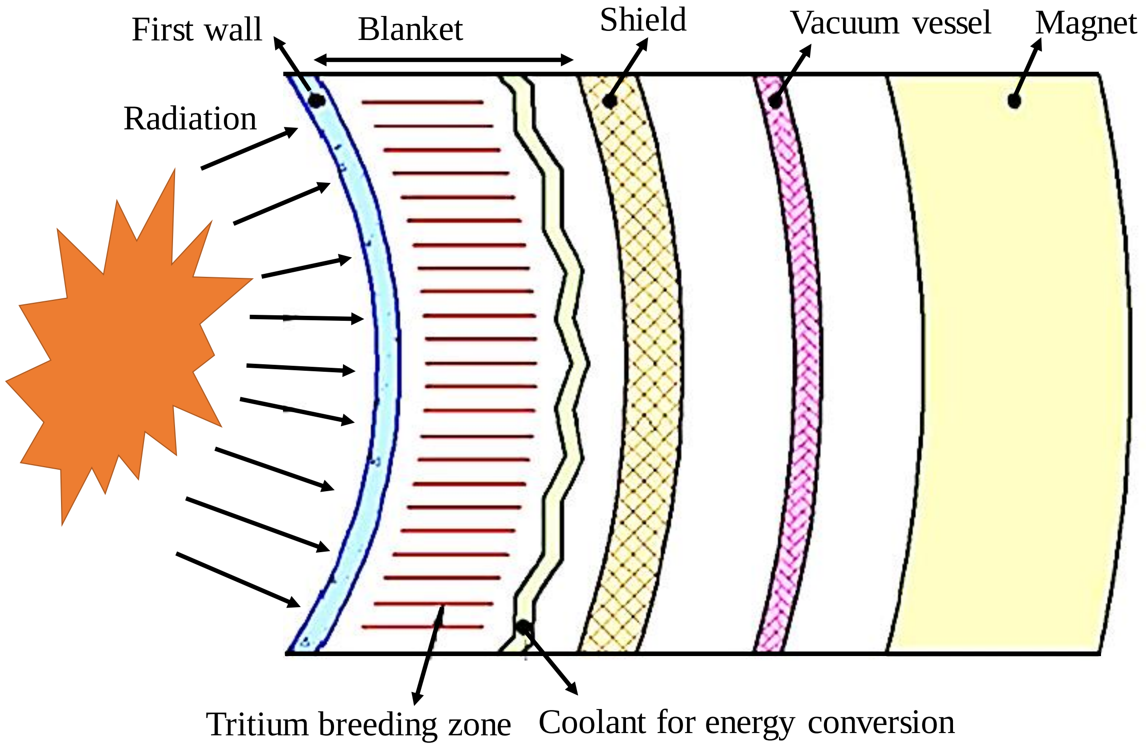
- **First wall** Structural Material
  - Reduced activation ferritic martensitic steel (ITER)

- **Lead-Lithium cooled Ceramic Breeder (LLCB)**
  - Eutectic Lead Lithium Alloy – (Coolant , neutron multiplier and T breeder)
  - Lithium Titanate- solid breeder

$$n + Li^6 \rightarrow T + He$$



Materials of Construction In FUSION Concept (ITER)



Key issues of Pb-Li cooled blankets in ITER

- Tritium permeation,
- Corrosion and
- Magneto-hydrodynamic drag (MHD) effects

Possible solutions : Ceramic coatings

- ❖ Prevents direct contact of the materials with the liquid metal
- ❖ Electrically decouple from conductive liquid metal flowing in the magnetic field

Proposed Coatings

- Oxides ($A1_2O_3$, Cr_2O_3, Y_2O_3, SiO_2, CaO and MgO)
- Nitrides (A1N, TiN)
- Carbides (β-SiC, TiC)

Why Al_2O_3 Preferred ?

- Thermochemical stability
- High electrical resistivity
- Radiation stability
- Compatibility with Pb-Li alloy

Reactor Operating Conditions and compatibility issues

- **Temperature**
  - Maximum 500°C (Majorly limited by Structural Material Selection !!!)

- **Intense Radiation Environment**
  - High Energy Neutron Flux (14.1 MeV)
  - Estimated DPA (150 – 1000)

→ Displacement Damage → Neutron Transmutation → Phase Instability → Swelling

- **Compatibility between coolant and coatings**

→ **T permeation, MHD, corrosion of structural materials**

In ITER at operating temperature of 450-550°C, the compatibility of alumina with the liquid Pb-Li alloy is a critical factor.

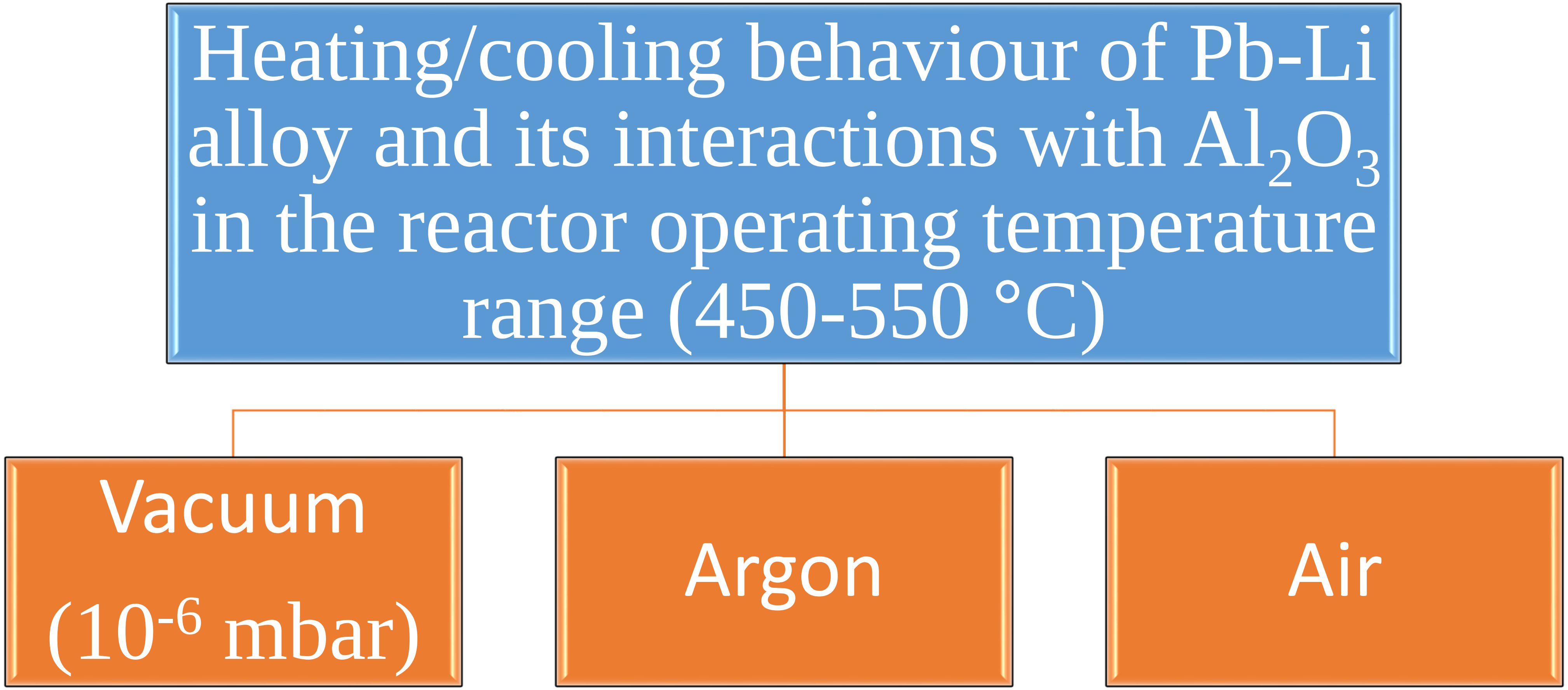
- Hubberstey et.al reported the formation of Li_2O(s) in Pb-Li alloy in presence of oxygen despite the low activity of Li.

- In their thermodynamic calculations, they indicated that in oxygen saturated Pb-Li, oxides like alumina should be thermodynamically stable.

- Later, Pint et al have reported that the interaction of Pb-Li with alumina in argon atmosphere at 800 °C for 1000 h leads to the formation of $LiAlO_2$(s) compound .

- It may be noted in their study that kinetics of reaction was slow (1000 h). This can be attributed to the limited supply of oxygen (from impurity in argon or dissolved oxygen in Pb-Li).

Present study

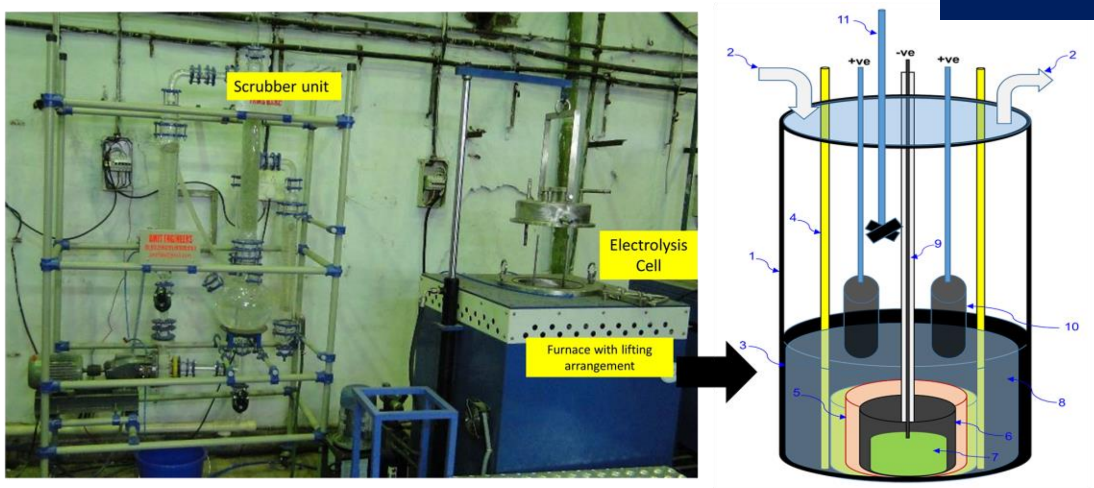


In-house Developemnt of eutectic Pb-Li

Fused salt electrolysis process for Pb-Li alloy

- Process development for the synthesis of dilute Pb-Li alloy using LiCl as a source of Lithium
- Demonstrate the commercial viability of developed process by scaling it in 20 Kilogram level

Production Setup



$Li^+ + e^- \rightarrow Li\,(Pb)$ (*on liquid lead cathode*)

$2Cl^- \rightarrow Cl_2 + 2e^-$ (*graphite rod-anode*)

The schematic of fused salt electrolysis assembly for lead lithium preparation

Pb-Li Alloy

1	Retort
2	Gas connectors
3	High density graphite for holding molten salt
4	Cage
5	Recrystallized alumina crucible
6	High density graphite for holding molten lead
7	Molten lead (cathode)
8	Molten LiCl-KCl
9	Cathode
10	Anode
11	Mechanical Stirrer assembly

- **Patented technology** (PCT/IB2018/056434, European Patent (18773618.6-1108)), August 2022

Interaction studies of alumina with Pb-Li alloys

1. **Heating Pb-Li alloy in an alumina boat**

   (550 °C for 6 h in the flowing high purity argon atmosphere)

2. **Thermal equilibration of Pb-Li alloy with alumina powder**

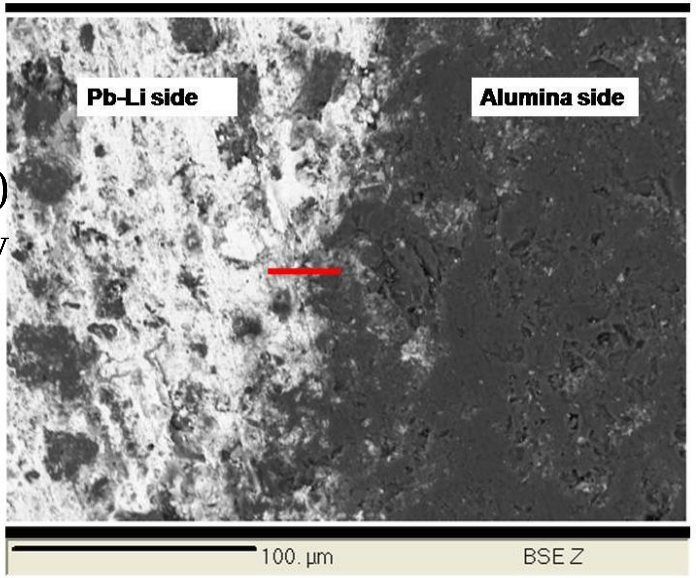
   (Pb-Li alloy was mixed with alumina powder kept at 550 °C for 48 h in vacuum and air both)

3. **Thermal analysis studies (TG-DTA)**

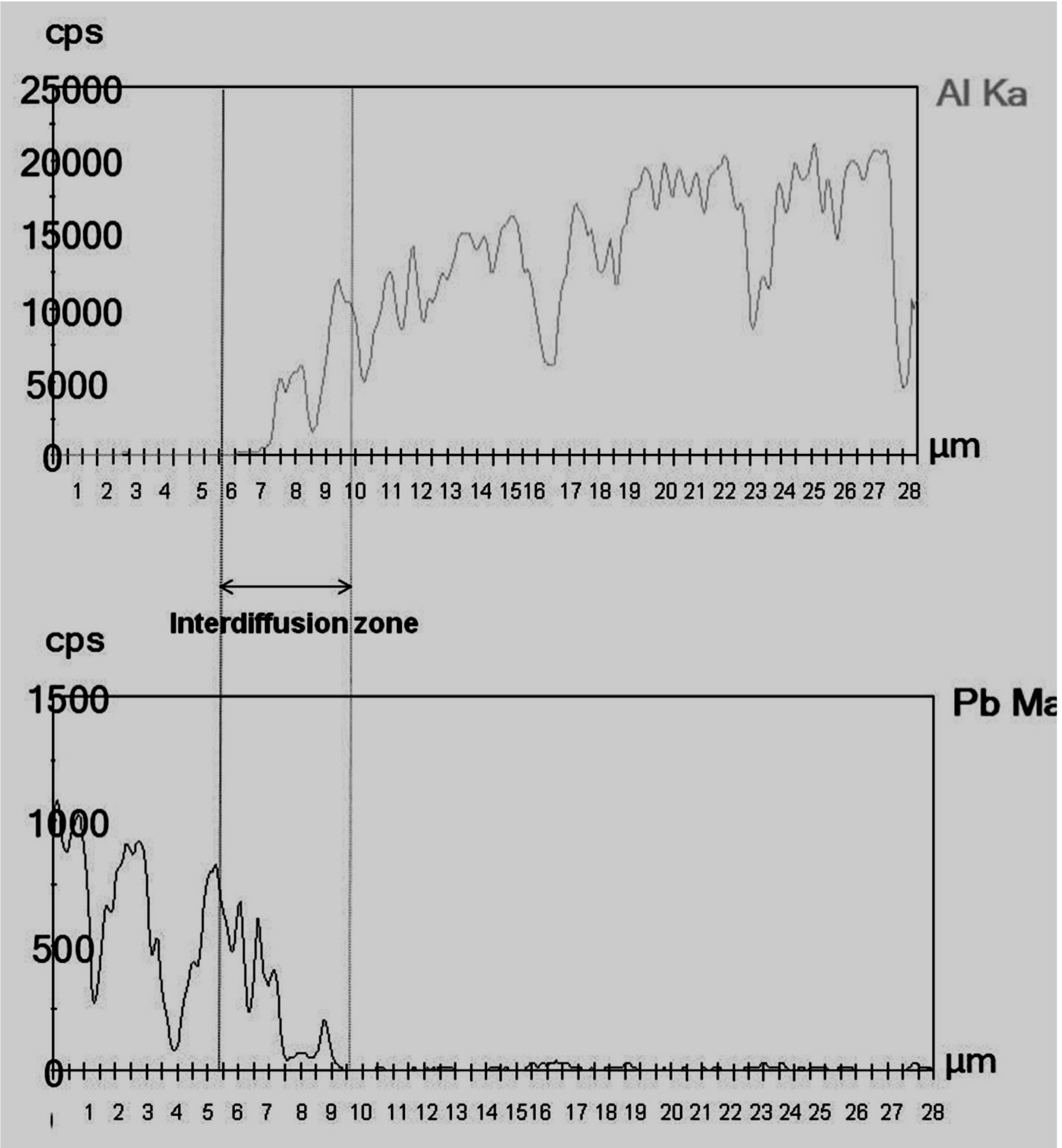
   (Heated in Setaram Thermoanalyzer from 50°C to 500 °C at a heating rate of 5°C/min in an alumina cup both under flowing high purity argon atmosphere and in air)

Heating Pb-Li alloy in an alumina boat

- Interaction studies were initially done by melting Pb-Li alloy in an alumina boat at 550 °C for 6 h in the flowing argon (high purity) atmosphere.
- Solidified melt was found sticking to the surface of alumina boat. Interface of alumina and solidified Pb-Li was compositionally analyzed by Electron Probe Micro Analyzer (EPMA).
- Inter-diffusion zone of width around 4μm where counts corresponding to both lead and aluminum were present. The inter diffusion of both Pb and Al indicates the possibility of interaction of Pb-Li with Al_2O_3.



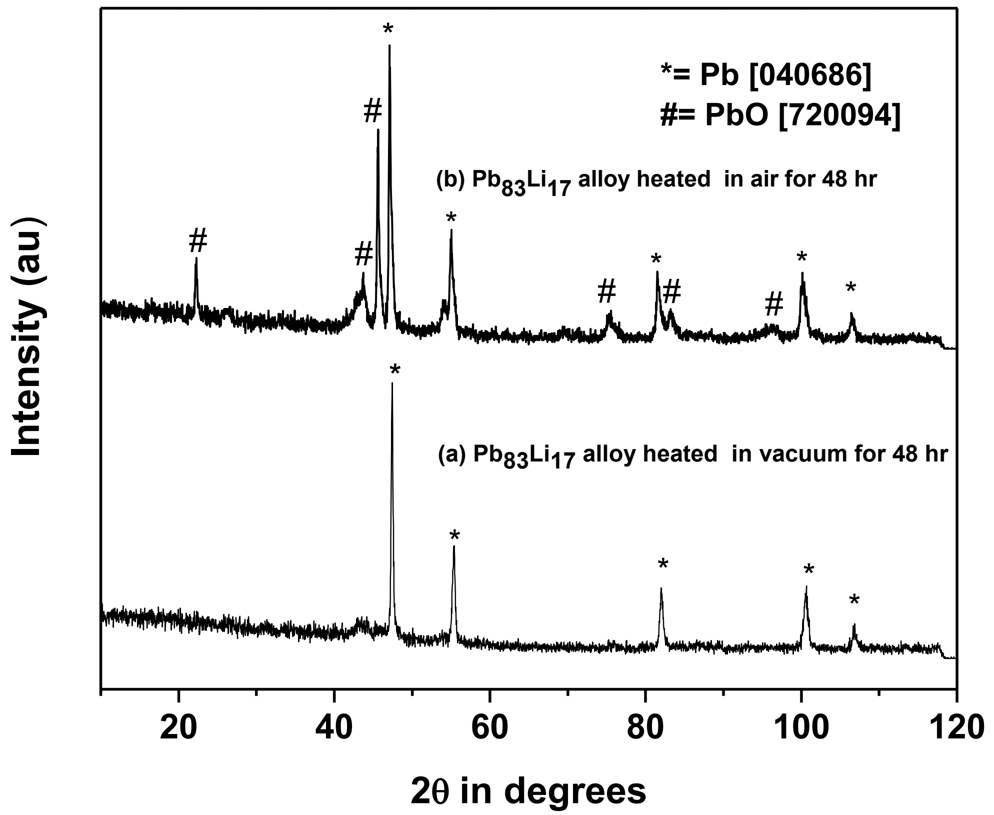
Back scattered electron (BSE) EPMA image of Pb-Li alloy and alumina interface



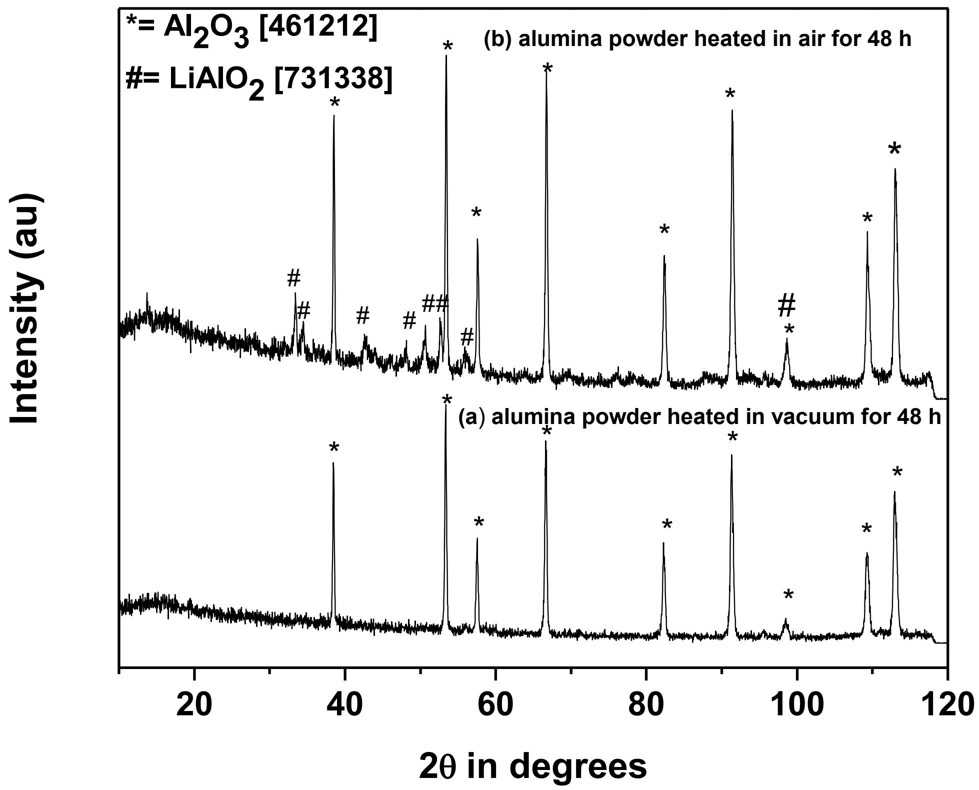
EPMA line scans of Pb-Li alloy and alumina interface depicting Al and Pb counts

Thermal equilibration studies

XRD patterns of Pb-Li alloy thermally equilibrated with alumina powder at 550°C for 48h in vacuum (4×10^{-6} mbar pressure) and in air



XRD patterns of lead lithium alloy thermally equilibrated with alumina powder at 550°C for 48h (a) in vacuum (b) in air



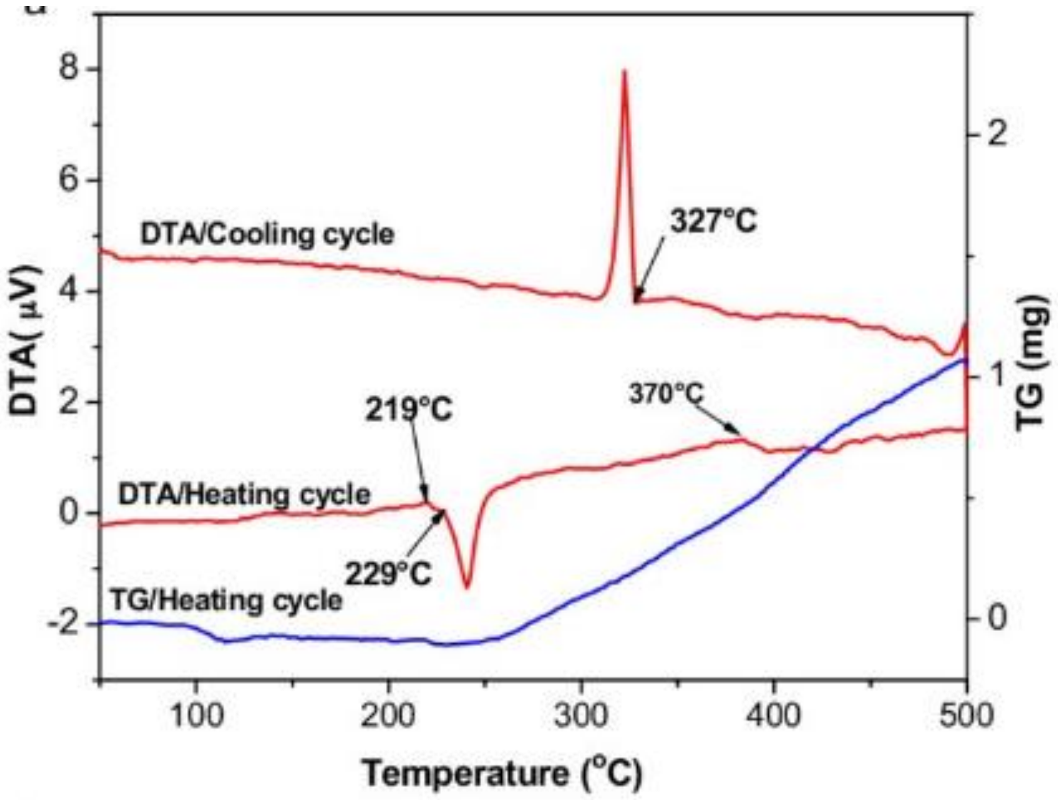
XRD patterns of alumina thermally equilibrated with lead lithium alloy at 550°C for 48h (a) in vacuum (b) in air

- Sample equilibrated in air showed peaks due to $LiAlO_2$ phase in addition to the alumina peaks.
- These observations indicate that at 550 C Al_2O_3 interacts with $Pb_{83}Li_{17}$ alloy in presence of oxygen as per the reaction:

$$Li_2O(s) + Al_2O_3(s) = 2LiAlO_2(s) \ (\Delta G°_{550°C} = -117 \text{ kJ})$$

Thermal Analysis (TG-DTA) Studies

In flowing Argon Gas Atmosphere



Peak temperature	Event
219 °C	Magnetic transition of PbLi
229 °C	Eutectic melting of Pb-Li
230 °C to 500 °C (in TG)	Oxidation of entire Li in Pb-Li alloy (1.25 mg wt. gain)
327 °C	Freezing of liquid Pb.

Preferential oxidation of Li metal in the molten Pb-Li alloy in the temperature range 230 to 500 °C (beyond the eutectic melting)

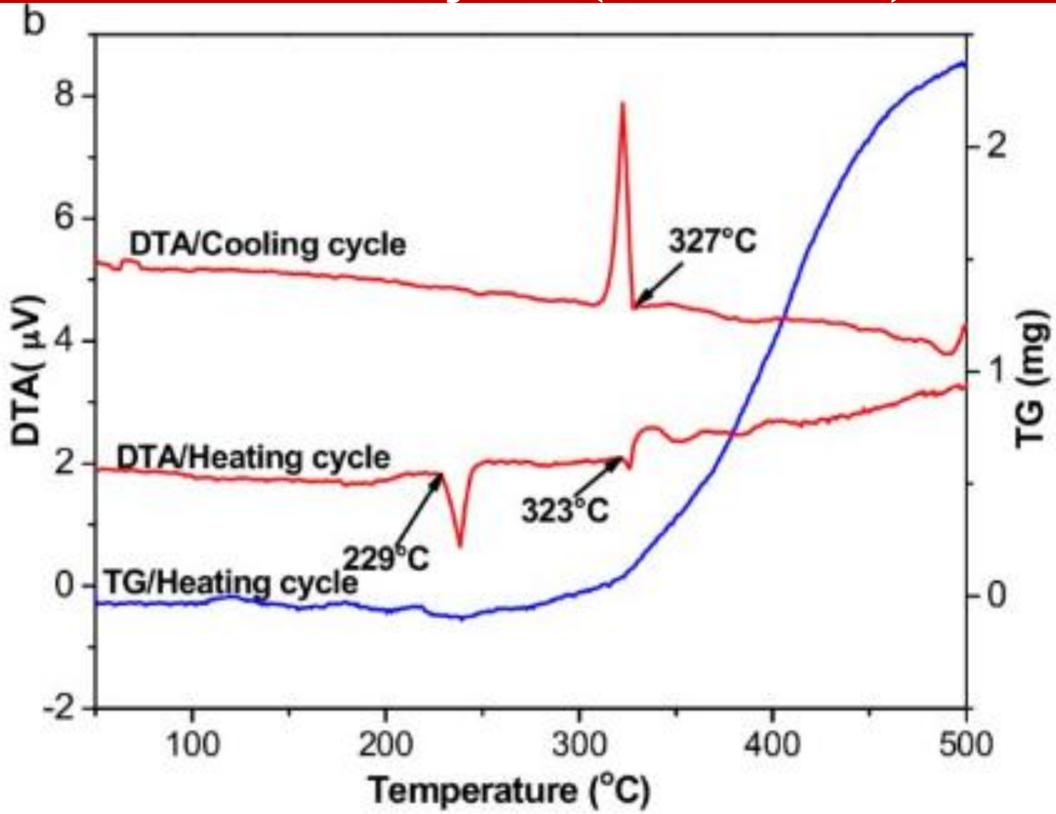
Good agreement with the expected mass gain (1.26 mg) if the entire Li in 170 mg Pb-Li alloy was considered to be oxidised.

Oxidation of Li observed in flowing argon can be explained on the basis of the equilibrium oxygen potential of Li/Li_2O system which is 10^{-61} atm at 220 °C, suggests that the oxygen potential achieved by the flow of argon in the system is far too excess than required oxygen potential.

Cooling curve recorded for the system gives a single exothermic peak at 327 °C, which could be due freezing of liquid Pb.

Thermal Analysis (TG-DTA) Studies

In Oxygen Atmosphere



Peak temperature	Event
229 °C	Eutectic melting of Pb-Li
323 °C	melting of Pb
230 to 500 °C (in TG)	Oxidation of entire Li and partially Pb also (2.5 mg wt. gain)
327 °C	due freezing of liquid Pb

DTA peak at 323 °C recorded in air can be attributed to the melting of Pb metal formed due to the preferential oxidation of Li-component at even lower temperature (when compared to the argon heated sample).

This observation is also supported by the mass gain curve in the TG plot, which shows 2.5 mg mass gain for 170 mg sample in the temperature range 230 to 500 °C when heated

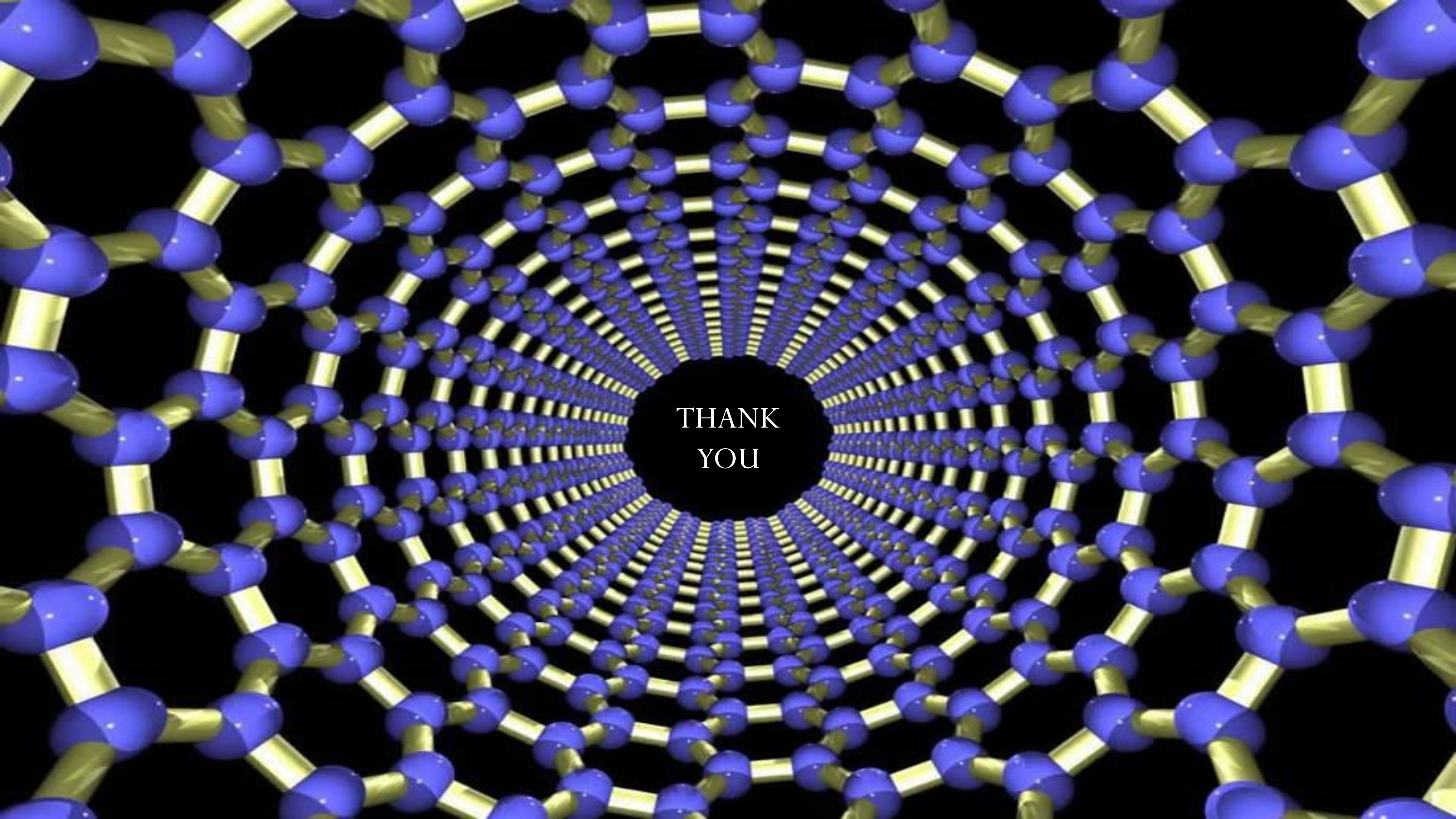
From the total mass gain of 2.5 mg in the TG plot a mass of 1.26 mg is attributed to the complete oxidation of Li (17 at %) forming Li_2O(s) and the rest (1.24 mg) is due to partial oxidation of lead forming PbO (s).

DTA plot in the cooling cycle due to Pb freezing is relatively less intense due to freezing of Pb(l) has decreased correspondingly as compared to the argon heated sample which shows that less amount of metallic Pb was present in this alloy.

Summary

Interaction of liquid Pb-Li alloy with Al_2O_3 at the operating temperature of the fusion reactors (400-550 °C) was studied. Role of oxygen in the interaction was also studied. Following are the major observations:

- Under vacuum (4×10^{-6} mbar) at 550 °C for 48 h there was no interaction of liquid Pb-Li alloy with Al_2O_3.
- In air, at 550 °C for 48 h, both lead and lithium in liquid Pb-Li alloy was oxidised. Even in flowing argon, there was rapid oxidation of lithium in liquid Pb-Li alloy beyond the eutectic melting temperature (235°C).
- It was seen that alumina reacts with Li_2O at 550 °C to form $LiAlO_2$ compound. The reaction is rapid in the presence of oxygen and happens more slowly in the presence of flowing argon.


THANK
YOU

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