Corrosion susceptibility of structural materials for fusion in liquid and solid breeders

Master Thesis
presented by

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Abstract

Tritium is produced by the reaction between lithium and neutron in a component known as breeding blanket for the operation of a fusion reactor with DT cycle. The European Union has developed 2 Test Blanket Modules (TBMs): Helium Cooled Lithium Lead (HCLL) and Helium Cooled Pebble Bed (HCPB). The structural material is RAFM steel EUROFER and the breeding materials are eutectic lead-lithium and lithium ceramic pebbles. The compatibility of structural materials in both liquid and solid breeders is an essential issue of fusion research. The objective of this thesis is a systematic study of corrosion susceptibility of structural materials in liquid and solid breeders with literature review and corrosion experiments carried out at Ciemat.

A lot of lead-lithium testing loops are built to perform corrosion tests most of which are in dynamic condition. The main corrosion mechanism is dissolution of steel alloying elements into liquid lead-lithium. The corrosion rate is dependent on temperature, flow velocity and magnetic field. At the required temperature the reduction of flow velocity decreases the corrosion rate. The magnetic field enhances the corrosion rate and forms furrow structure on the steel surface that may change the mechanical properties. Application of corrosion resistant coatings is one possible way to reduce the corrosion rate.

The study of corrosion behavior of structural material in solid ceramic breeder is very limited so far. The corrosion mechanism is complex and still needs to be studied clearly. The analyses of lithium ceramic pebbles show the contamination of steel alloying elements on the surface. Different spatial distributions of alloying elements are in accordance with the expected formation of oxidation products. The surface color of EUROFER sample changes after the corrosion tests carried out at Ciemat. The analyses of tested EUROFER sample show the formation of two oxidation layers with different morphology on the surface.
## Contents

1 Introduction ........................................................................................................... 5  
   1.1 Background of Fusion .............................................................................. 5  
   1.2 Fusion Materials ...................................................................................... 7  
      1.2.1 Structural materials ......................................................................... 8  
      1.2.2 Plasma facing materials .................................................................. 9  
      1.2.3 Functional materials ....................................................................... 9  
   1.3 ITER TBM program ................................................................................... 10  
      1.3.1 Test Blanket Systems ...................................................................... 10  
      1.3.2 The European Union TBSs ................................................................. 11  
   1.4 Objective of Thesis ................................................................................... 12  

2 Corrosion behavior in eutectic Pb-Li ............................................................... 15  
   2.1 Eutectic composition ................................................................................ 15  
   2.2 Experimental tests and results ................................................................. 16  
      2.2.1 A thermal convection loop TULIP in Italy ...................................... 17  
      2.2.2 A forced circulation loop in USA ................................................... 18  
      2.2.3 A forced circulation loop PICOLO in Germany ............................ 19  
   2.3 Corrosion mechanism ............................................................................. 21  
   2.4 Effect of temperature and flow velocity ................................................. 23  
   2.5 Effect of magnetic field ......................................................................... 25  
   2.6 Improvement proposals .......................................................................... 30  

3 Corrosion behavior in ceramics .................................................................... 33  
   3.1 Corrosion mechanism ............................................................................ 33  
      3.1.1 Solid state reaction ........................................................................... 33  
      3.1.2 Oxidation mechanism of steels ......................................................... 34  
   3.2 Previous study review ........................................................................... 35  
   3.3 Experiments at Ciemat .......................................................................... 39  
      3.3.1 Experimental setup and procedure .................................................. 39  
      3.3.2 Results and discussions .................................................................. 41  

4 Conclusions ...................................................................................................... 43  
   4.1 Conclusions ............................................................................................ 43  
      4.1.1 Corrosion behavior in eutectic Pb-Li ............................................... 43  
      4.1.2 Corrosion behavior in ceramics ....................................................... 43
4.2 Future work \hspace{2cm} 43
Chapter 1

Introduction

1.1 Background of Fusion

Of the world primary energy needs every year, only around 6% is supplied by the very low CO$_2$-emitting nuclear power [1]. All nuclear power stations in operation today rely on fission — the splitting of large atomic nuclei. Most nuclear power stations are fuelled by heavy element uranium. An alternative approach to have usable energy production depends on nuclear fusion. Nuclear fusion is a promising future energy source due to the short lived radioactivity of the produced waste, its low carbon emissions and its prospective power output. Fusion research holds out the promise of providing a clean, sustainable energy supply to contribute to the increasing needs of our civilization. Research into nuclear fusion to generate electricity is ongoing despite of huge technical challenges.

The basis of nuclear fusion is the release of energy when very light nuclei are brought together to form more stable heavier ones. The total binding energy of initial components is greater than that of reaction products, and it is this energy difference that is released during fusion. These small differences in binding energy are reflected in the observable masses of various reaction components, via Albert Einstein’s famous equation describing the equivalence of mass and energy: $E = mc^2$. The components after reaction actually weigh less than those before reaction and the mass difference is released as energy. Einstein’s equation gives an indication of the scale of proportionality between mass and energy, and it explains why very small changes of mass can release a great deal of energy.

The next fusion reactors will be based on the deuterium-tritium (D&T) reaction due to greater reaction cross section at lower temperature: $D + T \rightarrow He(3.5 MeV) + n(14.1 MeV)$. The reacting nuclei must collide hard and often to undergo fusion, and the requirements of multiple, high-energy collisions are met in a hot, dense plasma, i.e. thermonuclear fusion. The key problem in achieving thermonuclear fusion is how to confine the hot plasma. As high temperature of plasma implies high pressure, the plasma tends to expand and some force is necessary to act against this thermal pressure. This force can
be either gravitation in stars, magnetic forces in magnetic confinement fusion reactors, or the plasma’s inertia which keeps the material together so that fusion reaction may occur before the plasma starts to expand. Among them, the magnetic confinement approach is more highly developed and usually considered more promising. A variety of magnetic configurations exist, including toroidal geometries of tokamaks or stellarators and open-ended mirror confinement systems [2].

The roadmap towards a fusion reactor builds mainly on three devices: the Joint European Torus (JET), its successor the International Thermonuclear Experimental Reactor (ITER) and a DEMOnstration power reactor (DEMO). JET is currently the largest facility of experimental tokamak nuclear fusion reactor in operation and the only machine capable of operating with the deuterium-tritium fuel. In operation since 1983, JET was explicitly designed to study plasma behavior in conditions and dimensions approaching those required in a fusion reactor. Today its primary task is to prepare for the construction and operation of ITER, acting as a test bed. ITER is the world’s largest experimental tokamak nuclear fusion reactor currently being built at the Cadarache facility in the south of France. The ITER project aims to make the long-awaited transition from experimental studies of plasma physics to full-scale electricity-producing fusion power plants. DEMO is a proposed nuclear fusion power plant that is to build upon the expected success of ITER. A variety of countries in the world are starting to prepare a concrete conceptual design of DEMO. The main parameters of these three devices are listed in Tab. 1.1 [3–5].

<table>
<thead>
<tr>
<th>Device</th>
<th>JET</th>
<th>ITER</th>
<th>DEMO (JP, Ref. [5])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fusion Power</td>
<td>16 MW</td>
<td>500 MW</td>
<td>2.3 GW</td>
</tr>
<tr>
<td>Q factor</td>
<td>~0.7</td>
<td>10-20</td>
<td>&gt;30</td>
</tr>
<tr>
<td>Plasma major radius(R)</td>
<td>2.96 m</td>
<td>6.2 m</td>
<td>5.8 m</td>
</tr>
<tr>
<td>Plasma minor radius (a)</td>
<td>1.25 m</td>
<td>2.0 m</td>
<td>1.45 m</td>
</tr>
<tr>
<td>Plasma current</td>
<td>4.8 MA</td>
<td>15 MA</td>
<td>12 MA</td>
</tr>
<tr>
<td>Magnetic field</td>
<td>3.5 T</td>
<td>5.3 T</td>
<td>9.5 T</td>
</tr>
<tr>
<td>Length of pulses</td>
<td>60 s</td>
<td>300-500 s</td>
<td>&gt;1000 s</td>
</tr>
<tr>
<td>Neutron wall load</td>
<td>60 kW/m²</td>
<td>0.57 MW/m²</td>
<td>3 MW/m²</td>
</tr>
</tbody>
</table>

Table 1.1: Main parameters of JET, ITER and DEMO.

Operation of a power plant with DT cycle requires introduction of an essentially continuous supply of deuterium and tritium into reactor chamber. Deuterium is readily available as heavy water (D₂O) on earth from which deuterium can be separated by simple electrolysis. However, naturally occurring tritium is insufficient in quantity and concentration for use. In the current proposal, tritium can be produced by the reaction between lithium and neutron
1.2 Fusion Materials

in a component known as “breeding blanket”. Naturally occurring lithium is composed of two stable isotopes, \(^6\text{Li}\) and \(^7\text{Li}\), the latter being the more abundant (92.5% natural abundance). The nuclear reaction to produce tritium is

\[
\overset{6}\text{Li} + n \rightarrow ^4\text{He} + T + 4.8\text{MeV}, \quad \overset{7}\text{Li} + n_{\text{fast}} \rightarrow ^4\text{He} + T + n_{\text{slow}} + 2.5\text{MeV}.
\]

From Fig. 1.1, the cross section is much greater for \(^6\text{Li}\) at relatively low energy of neutron. As result, breeding material enriched in \(^6\text{Li}\) can significantly enhance tritium production.

![Li-6(n,\alpha)t and Li-7(n,n,\alpha)t Cross-Section](image)

**Figure 1.1:** Cross-section of Li-6(n,\alpha)t and Li-7(n,n,\alpha)t.

### 1.2 Fusion Materials

In fusion reactors, the plasma facing (first wall, divertor) and breeding blanket components will be exposed to plasma particles and electromagnetic radiation and will suffer from irradiation by an intense flux of 14 MeV neutrons. The high-energy fusion neutrons will produce atomic displacement cascades and nuclear transmutation reactions within the irradiated materials. They also will suffer from strong magnetic field, high heat flux and mechanical loads.

The first wall will consist of a structural material attached to a plasma facing (or armor) material. The breeding blanket will consist of a neutron multiplier, a tritium breeding material, one or several coolants, and a structural material to separate and contain the different materials. The divertor will consist of a structural material (heat sink) containing a coolant and supporting a plasma facing (or armor) material. Three types of materials are of primary concern: the plasma facing materials, which will serve as an armor for the underlying materials; the functional materials, which will have one or several particular functions (e.g. tritium breeding, neutron multiplication, optical
transmission, etc); and the structural materials, which will support the basic structure of the reactor. The main candidate materials for fusion are listed in Tab. 1.2 [6].

<table>
<thead>
<tr>
<th>Function</th>
<th>First wall</th>
<th>Breeding blanket</th>
<th>Divertor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma facing material</td>
<td>W-based alloy, W-coated</td>
<td>W-based alloy, W-coated</td>
<td></td>
</tr>
<tr>
<td>Neutron multiplier material</td>
<td>ODS steel, flowing liquid</td>
<td>SiC/ SiC&lt;sub&gt;f&lt;/sub&gt;, flowing liquid</td>
<td></td>
</tr>
<tr>
<td>Tritium breeding material</td>
<td>Be, Be&lt;sub&gt;12&lt;/sub&gt;Ti, Be&lt;sub&gt;12&lt;/sub&gt;V, Pb</td>
<td>Li, eutectic Pb-Li, Li-based ceramic material (Li&lt;sub&gt;2&lt;/sub&gt;O, Li&lt;sub&gt;4&lt;/sub&gt;SiO&lt;sub&gt;4&lt;/sub&gt;, Li&lt;sub&gt;2&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;, Li&lt;sub&gt;2&lt;/sub&gt;ZrO&lt;sub&gt;3&lt;/sub&gt;, LiAlO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>metal Li, Ga, Sn, Sn-Li</td>
</tr>
<tr>
<td>Structural material</td>
<td>RAFM steel, ODS steel, V-based alloy, SiC/ SiC&lt;sub&gt;f&lt;/sub&gt;</td>
<td>RAFM steel, ODS steel, V-based alloy, SiC/ SiC&lt;sub&gt;f&lt;/sub&gt;</td>
<td>ODS steel, W-based alloy</td>
</tr>
<tr>
<td>Coolant</td>
<td>Water, Helium, eutectic Pb-Li, liquid metal Li</td>
<td>Water, Helium</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2: Main candidate materials for fusion.

### 1.2.1 Structural materials

The qualification of structural materials is a fundamental challenge. They will be exposed to high temperatures and high levels of neutron irradiation, as well as to high mechanical and thermo-mechanical stresses. In addition, the thermal efficiency of a reactor, according to the Carnot cycle, is proportional to the difference between the outlet temperature of the coolant and the inlet temperature of the coolant. These temperatures are mainly limited by the temperature window for use, i.e. the window of operation of the structural materials, which is mainly limited by their mechanical properties under irradiation.

Candidate structural materials have a chemical composition that is based on low activation chemical elements (Fe, Cr, V, Ti, W, Si, C), including Reduced Activation Ferritic/Martensitic (RAFM) steels, Oxide Dispersion Strengthened (ODS) RAFM and ODS Reduced Activation Ferritic (RAF) steels, tungsten-based alloys, vanadium-based alloys and fibre reinforced SiC/SiC<sub>f</sub> ceramic composites. Each alternative alloy class exhibits specific problems arising from their intrinsic properties and from their resistance to radiation damage. For the time being, the most promising structural materials for future fusion power reactors seem to be the RAFM steels for which the greatest technology maturity has been achieved, i.e. qualified fabrication routes, welding technology and a general industrial experience are available. Their temperature window of use is presently about 625–825 K, the lower temperature being limited by irradiation-induced embrittlement effects and the upper temperature by a strong drop in mechanical strength. However, a difference of 200 K between
the outlet and inlet temperatures of the coolant should be sufficient to ensure acceptable efficiency of first generation fusion power reactors.

In Europe, Japan and Russia it has been demonstrated that it is now feasible to produce RAFM steels on an industrial scale with sufficiently low impurity levels. Main RAFM steels that are being investigated include the Chinese CLAM and CLF-1 alloys, the European EUROFER 97 alloy, the Japanese F82H and JLF-1 alloys, and the Russian RUSFER-EK-181 alloy. Their composition lies in the following range: Fe-(7.5–12)Cr-(1.1–2)W-(0.15–0.25)V, in weight percent [6].

1.2.2 Plasma facing materials

The qualification of plasma facing materials is very demanding. Plasma facing materials will be directly exposed to the fusion plasma which means that they will be exposed to high temperature, high heat flux of energetic particles, neutron irradiation and electromagnetic radiation, sputtering erosion, etc. The selection of plasma facing materials is mainly limited by their capability for absorbing heat and minimizing plasma contamination.

The main candidate plasma facing materials are refractory metals and alloys, like tungsten-based alloys, which have the advantage of high melting point, high thermal conductivity and high threshold for physical sputtering energy. An alternative to the use of high-melting-point materials would consist in using flowing liquid metal as plasma facing material. Flowing liquids have high heat load capability and could allow simultaneous heat and particle removal [6].

1.2.3 Functional materials

The qualification of functional materials is also very demanding. Their mechanical resistance under irradiation is presently considered of no primary concern. However, material properties like the tritium release behavior, thermal conductivity and structural integrity after prolonged neutron irradiation are important concerns. As compared to structural materials, orders of magnitude more hydrogen and helium isotopes will be generated in functional materials, e.g. in beryllium-type neutron multipliers and lithium ceramic-type tritium breeders. The irradiation resistance of other functional materials, such as ceramic insulators, dielectric and optical windows, optical fibers or complete sensor assemblies, is also an important concern.

The lack of adequate functional materials enabling a very high temperature design window is an important issue for fusion power reactors. Component lifetime will be determined by the resistance of functional materials as well as plasma facing materials and structural materials. Unfortunately, the choice of functional materials is very limited, as it relies mainly upon the properties require by the envisaged function [6].
1.3 ITER TBM program

A tritium breeding blanket (BB) ensuring tritium breeding self-sufficiency is a compulsory component for DEMO, the next-step after ITER, although is not present in ITER. Mock-ups of DEMO BB, called Test Blanket Modules (TBMs), will be inserted and tested in ITER in three dedicated equatorial ports (#02, #16, #18) directly facing the plasma. Each port can accommodate two TBM-SetS, therefore six TBMs and associated independent systems can be tested in ITER. They are the principal means by which ITER will provide the first experimental data on the performance of the BBs that is still an open issue on the path to commercial fusion power. These activities correspond to the so-called “TBM Program”. A successful ITER TBM Program represents an essential step on the path to DEMO for any fusion power development plan.

1.3.1 Test Blanket Systems

Six mock-ups of six whole DEMO-BB systems will be tested in ITER, which means that the TBMs are connected with several ancillary systems, such as cooling systems, tritium extraction systems, coolant purification systems, and instrumentation and control (I&C) systems. TBMs and associated systems are called Test Blanket Systems (TBSs). The TBSs functional characteristics are dictated by the operational conditions and requirements expected in a DEMO-BB system and, in this sense, they differ from the other ITER components that are designed in compliance with only ITER requirements. However, they must be fully integrated in ITER; therefore they must be compatible with the systems and operational procedures of ITER and the ITER operating plan. Moreover, TBS testing must not endanger ITER performances, safety, and availability. All ITER members contribute to the TBM program. At present, the following six independent TBSs are used for the integration and interfaces definition in ITER:

- the Helium Cooled Lithium Lead (HCLL) TBS and the Helium Cooled Pebble Bed (HCPB) TBS for installation in Equatorial Port #16;
- the Water Cooled Ceramic Breeder (WCCB) TBS and the Dual Coolant Lithium Lead (DCLL) TBS for installation in Equatorial Port #18;
- the Helium Cooled Ceramic Breeder (HCCB) TBS and the Lithium Lead Ceramic Breeder (LLCB) TBS for installation in Equatorial Port #02. The typical dimensions of each TBM are: 1.66 m (poloidal) × 48 cm (toroidal) × 50/70 cm (radial). The structural material for all TBMs is RAFM steel, which is a ferromagnetic material and therefore has an impact on the magnetic field close to the corresponding equatorial ports. The lead-lithium-based concepts use the liquid metal eutectic Pb-Li with melting temperature of 235 °C. The ceramic-based concepts use pebble-beds of either Li$_4$SiO$_4$ or Li$_2$TiO$_3$. In the Tab. 1.3 are listed what are used for structural, breeding material, neutron multiplier and coolant for six TBSs designs [7–13].
1.3 ITER TBM program

<table>
<thead>
<tr>
<th>TBM</th>
<th>Structural material</th>
<th>Breeding material</th>
<th>Neutron multiplier</th>
<th>Coolant</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCLL(EU)</td>
<td>EUROFER 97</td>
<td>eutectic Pb-Li (90% (^6)Li enrichment)</td>
<td>Eutectic Pb-Li</td>
<td>Helium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li(_2)SiO(_4) (reference, 30% (^6)Li enrichment) or Li(_2)TiO(_3) (60% (^6)Li enrichment) pebbles</td>
<td>Beryllium pebbles</td>
<td>Helium</td>
</tr>
<tr>
<td>HCPB(EU)</td>
<td>EUROFER 97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WCCB(JP)</td>
<td>F82H</td>
<td></td>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>DCLL(US/KR)</td>
<td>F82H</td>
<td></td>
<td></td>
<td>Helium and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>eutectic Pb-Li</td>
</tr>
<tr>
<td>HCCB(CN)</td>
<td>CLF-1</td>
<td></td>
<td></td>
<td>Helium</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLCB(IN/RU)</td>
<td>IN-RAFMS</td>
<td></td>
<td></td>
<td>Helium and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>eutectic Pb-Li</td>
</tr>
</tbody>
</table>

Table 1.3: Main candidate materials for fusion.

1.3.2 The European Union TBSs

The EU has developed two reference tritium breeder blankets concepts for future DEMO reactor that will be tested in ITER under the form of TBSs located in the Equatorial Port #16 of ITER: the Helium-Cooled Lithium-Lead (HCLL) TBS and the Helium-Cooled Pebble-bed (HCPB) TBS.

The EU TBSs are mainly subdivided in a set of sub-systems (SS): specific SSs for the HCLL, specific SSs for the HCPB, and common SSs. Fig. 1.2 shows the proposed sub-system breakdown for the EU TBSs. The SSs grouped under “HCPB specific SSs” are the HCPB TBM-Set, the HCPB Helium Coolant System (HCS), the HCPB Tritium Extraction System (TES), the HCPB Coolant Purification Systems (CPS) and the HCPB Data Acquisition and Control System (DACS). Under the “HCLL specific SSs” analogous systems are grouped, like the HCLL TBM-Set, the HCLL HCS, the HCLL CPS and the HCLL DACS. To this list few HCLL specific SSs are added, like the PbLi loop and the Tritium Removal System (TRS), according to the different T extraction mechanism that is based on the external recirculation of the liquid PbLi. The equipment located in the port cell (PC) #16, namely the Auxiliary Equipment Unit (AEU) Structure, the Pipe Forest (PF) and the PC Equipment, has been grouped under “common SSs”. Also the Equipment in the Hot Cell Facility (HCF), namely the Hot Cell Equipment (HCE), is part of this group [9].

The EU TBMs concepts have been designed from a joint CEA/KIT work. Fig. 1.3 shows an exploded view of these two TBMs. The TBMs are connected to a TBM shield to form the TBM-Set. Both TBM-Sets are integrated in TBM Port Plug (PP) illustrated in Fig. 1.4 [9].

Both TBMs are using 9Cr-WVTa RAFM steel, the EUROFER, as structural material. The HCLL uses the breeder/multiplier material in form of a liquid Pb-Li in the quasi-eutectic composition (PbLi\(_{eq}=15.7\) at% Li, denoted as Pb-15.7Li) with 90% \(^6\)Li enrichment. The liquid Pb-Li slowly flows from the TBM to the port cell in order to extract the produced tritium. It is
cooled by Helium at a pressure of 8 Mpa and inlet/outlet temperatures of 300°C/500°C. The HCPB uses a ceramic breeder in the form of pebble beds as tritium breeding material. Presently, lithium orthosilicate (OSi, Li₄SiO₄) with 30% ⁶Li enrichment and lithium metatitanate (MTi, Li₂TiO₃) with 60% ⁶Li enrichment are considered, OSi as the reference material, MTi as a back-up solution. It also uses Beryllium pebbles as neutron multiplier to increase the tritium breeding ratio performance. The tritium is produced in lithium ceramic pebbles with neutron irradiation and then recovered from the surface of pebbles by a purge gas which contains hydrogen and helium, composition is mainly He + 0.1% H₂ gas. The presence of 0.1% H₂ in the helium purge gas can enhance the release of tritium from the lithium ceramic. Maximum temperatures are 920°C in ceramics, 650°C in Be, and 550°C in steel. It is cooled by Helium at a pressure of 8 Mpa and inlet/outlet temperatures of 300°C/500°C [7,8].

1.4 Objective of Thesis

The chemical compatibility of breeding materials and structural materials is essential for safe and reliable system operation in nuclear fusion reactor. The compatibility issue is mainly relied on corrosion behavior between breeding materials and structural materials as it can affect the properties of structural materials and lifetime of TBMs due to changes in the microstructure, composition and surface morphology.

The main objective of this thesis is a systematic study of corrosion susceptibility of structural materials for fusion in liquid and solid breeders.

For liquid breeders with eutectic Pb-Li as tritium breeding material and
1.4 Objective of Thesis

neutron multiplier, the corrosion of structural materials is a critical challenge in the use of liquid lead-lithium alloy. The corrosion rate can be hundreds of micrometer per year and it can affect the properties of structural materials. A large number of corrosion tests had been carried out and lots of papers had been published in past thirty years. This thesis did a historical overview of most corrosion tests and discussed the effect of some operating parameters.

For solid breeders, however, the study is limited so far. Although it is expected that the corrosion degradation caused by solids is much lower than that due to liquid, it is still not negligible and should be evaluated properly. This thesis collected recent research results and did an experimental study of corrosion tests carried out at CIEMAT, Spain.
1. Introduction
Chapter 2

Corrosion behavior in eutectic Pb-Li

The chemical compatibility of breeding materials and structural materials is essential for safe and reliable system operation in nuclear fusion reactor. The compatibility issue is mainly relied on corrosion behavior between breeding materials and structural materials. Corrosion in the form of uniform or selective dissolution, inter-granular penetration, and interstitial-element transfer can result in significant wall-thinning/wastage and deposition of corrosion products that may cause severe flow restrictions and excessive accumulation of radioactive material in unshielded regions. The former consequence results in a loss of mechanical integrity and the latter phenomenon would increase requirements for pumping power, decrease the energy conversion efficiency, and complicate system maintenance [14].

This chapter starts from the evolution of eutectic composition and a historical overview of corrosion tests including operating parameters, kinds of structural materials and main results in past thirty years. Afterward we discuss the corrosion mechanism and effect of several setup parameters. At last we propose some improvements to reduce the corrosion effect of structural materials in eutectic Pb-Li.

2.1 Eutectic composition

Pb-Li eutectic is possible candidate for tritium breeding, cooling, and neutron multiplying functions in fusion reactor. Validated materials databases are needed for progress of any R&D technology. Among them, lithium concentration of the eutectic is a very important parameter. Lithium determines the eutectic chemical activity and fine variation of Li concentration can significantly vary the physical-chemical and solute transport properties. Quality assurance of Pb-Li eutectic is intimately related with the accurate determination of the eutectic chemical composition with the analysis technique certifying at 0.1% Li and the eutectic production technique guaranteeing its short-scale
homogeneity (in order to avoid Li aggregation) [15].

The only published data pertinent to the lead-rich section of the Pb-Li phase diagram ($x_{Li} < 25$ at%) are those on which Hansen and Anderko [16] based their compilation in 1958. In their book “Constitution of Binary Alloys”, they reviewed the previous work and recommended the most extensive and comprehensive data which was 17 at% Li (denoted as Pb-17Li) at melting point 235°C. Hence Pb-17Li became the choice of alternative breeder material for the blanket designs.

Liquidus temperatures are conventionally determined by thermal analysis methods. These methods, however, are unreliable since they suffer from the fact that, although non-equilibrium methods, they are used to determine equilibrium data. In 1992, Hubberstey and Sample [17] developed a new technique to redetermine the composition of Pb-Li eutectic. The measurement of electrical resistance as a function of temperature under equilibrium condition overcomes such problem, since the plots relating these two parameters, which are readily determined with a high degree of accuracy, exhibit an abrupt change in gradient at the liquidus and a sharp discontinuity at the eutectic. In their work, the eutectic composition corresponded to 15.7±0.2 at% (denoted as Pb-15.7Li) at melting point 235±1°C [17].

As a result the Pb-17Li alloy which was chosen for the most of conceptual designs of breeder blankets or experimental loops had been shown to lie. However, although this chemical composition differs a little from the eutectic one (Pb-15.7Li), it is not of great importance in practice and the alloy is still suitable for the operation of a blanket [18]. For the newest design proposal for EU HCLL TBM, the reference lead-lithium alloy is Pb-15.7Li.

### 2.2 Experimental tests and results

In past thirty years, large amount of corrosion tests were carried out on proposed structural materials in liquid Pb-Li loops [19–38].

The testing loops were in both static and dynamic conditions. The dynamic conditions included impeller/stirrer induced, thermal convection and forced circulation, etc. Several loops also contained a magnetic/cold trap to collect and remove the corrosion precipitates from flowing liquid metal. Among them, loop types of thermal convection and forced circulation are widely constructed by many countries.

The testing steel samples were exposed to liquid Pb-Li with various flow velocities at different temperatures. Afterward the tested samples were usually analyzed by measuring metal loss or length/diameter change, standard metallographic technique with optical microscopy, and by applying SEM (Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray spectroscopy) technologies, etc. Metal loss or length/diameter change can determine corrosion rates. Metallographic techniques can observe the surface morphology and roughness to determine corrosion attack. SEM/EDX analyses can investigate
2.2 Experimental tests and results

Among all the testing loops, three typical loops in which more than one corrosion tests were carried out are chosen to give an idea what the experimental loops look like and to discuss main test results. Other loops and tests are not described here in detail, further information please see Ref. [19–38].

2.2.1 A thermal convection loop TULIP in Italy

The schematic of TULIP is shown in Fig. 2.1. These square thermal convection loops ($0.5 \text{ m} \times 0.5 \text{ m}$) contained about one litre of Pb-17Li alloy and were heated along the lower horizontal leg and cooled by water jackets along the upper horizontal leg. Corrosion samples could be located in the isothermal hot leg and also in the heated leg [29].

![Figure 2.1: Schematic of TULIP (Ref. [29]).](image)

Figure 2.1: Schematic of TULIP (Ref. [29]).

The austenitic stainless steel 316 L and three types of martensitic or ferritic steels 1.4914, HT-9, T91 were tested in TULIP at Pb-17Li flow rate of
approximately 0.1 m/s and different temperatures. The main conditions are listed in Tab. 2.1.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Velocity (m/s)</th>
<th>Test temperature (°C)</th>
<th>Exposure time (h)</th>
<th>Sound metal loss (µm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>316 L</td>
<td>0.12</td>
<td>450</td>
<td>3000</td>
<td>54±5</td>
<td>[29]</td>
</tr>
<tr>
<td>1.4914</td>
<td>0.08</td>
<td>450</td>
<td>3000</td>
<td>7.5</td>
<td>[29]</td>
</tr>
<tr>
<td>1.4914</td>
<td>0.08</td>
<td>475</td>
<td>3000</td>
<td>13.9</td>
<td>[29]</td>
</tr>
<tr>
<td>1.4914</td>
<td>0.1</td>
<td>450</td>
<td>3000</td>
<td>7.2±1.1</td>
<td>[22]</td>
</tr>
<tr>
<td>HT-9</td>
<td>0.1</td>
<td>450</td>
<td>3000</td>
<td>7.2±0.4</td>
<td>[22]</td>
</tr>
<tr>
<td>T91</td>
<td>0.1</td>
<td>450</td>
<td>3000</td>
<td>6.15±0.35</td>
<td>[22]</td>
</tr>
</tbody>
</table>

Table 2.1: Experimental conditions and results of corrosion tests in TULIP loop.

To determine the corrosion behavior, loss of sound metal was measured. In the case of 316 L steel, loss of sound metal might be determined either by weight loss measurement after complete elimination of the ferritic layer or by thickness measurement of the ferritic layer on cross section micrographs. Both methods had been used. As for martensitic or ferritic steels, only weight loss might be used [29]. The different results are reported in Tab. 2.1 as well.

From Tab. 2.1, the sound metal loss was much greater for 316 L steel than martensitic or ferritic steels at the same temperature and flow rate of approximately 0.1 m/s. That comes to conclusion that martensitic or ferritic steels have better corrosion resistance than austenitic ones.

2.2.2 A forced circulation loop in USA

The forced circulation loop needs pump to force liquid alloy to flow and becomes more complex. Early in 1980’s USA had constructed a force circulation loop whose schematic is shown in Fig. 2.2. The main loop consisted of a high temperature test vessel with a heat exchanger, a cold leg, a linear induction pump and flow meter. The liquid Pb-17Li alloy was prepared in a separate vessel and transferred into the loop. The total volume of the loop was about two litres [19].

Corrosion steel samples, Type 316 stainless steel and ferritic HT-9 and Fe-9Cr-1Mo steels, were exposed to flowing Pb-17Li at 454°C and 427°C for up to 3300 h. The Pb-17Li alloy was recirculated at ~0.35 L/min and the cold leg temperature was maintained at 300°C. The steel samples also were tested at higher temperature 482°C for 1849 h.

The corrosion behavior was evaluated by measuring the change in weight of steel samples. The weight loss was found linear relationship with exposure time. The main experimental conditions and results are listed in Tab. 2.2.
2.2 Experimental tests and results

From the results we can find increasing corrosion rate with higher and higher test temperature. At the same temperature, the ferritic steels have better corrosion resistance than austenitic ones.

2.2.3 A forced circulation loop PICOLO in Germany

The PICOLO loop was a figure-of-eight type loop with a central heat exchanger, a hot leg and a cold leg. The cold leg contained the pump, flow meter and magnetic trap. The whole circuit was connected to a dry argon glove box as is shown in Fig. 2.3. The volume of PICOLO was about ten litres and the alloy was molten in the glove box and filled into the loop through the expansion vessel. The test section was a tube of 16 mm inner diameter and 440 mm length. Cylindrical samples of the materials to be tested were fixed in the
2. Corrosion behavior in eutectic Pb-Li

<table>
<thead>
<tr>
<th>Steel</th>
<th>Flow flux (L/min)</th>
<th>Test temperature (°C)</th>
<th>Exposure time (h)</th>
<th>Weight loss rate (mg m⁻²h⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-9, Fe-9Cr-1Mo</td>
<td>0.35</td>
<td>427</td>
<td>3300</td>
<td>4.7</td>
<td>[19]</td>
</tr>
<tr>
<td>HT-9, Fe-9Cr-1Mo</td>
<td>0.35</td>
<td>454</td>
<td>3300</td>
<td>7.2</td>
<td>[19]</td>
</tr>
<tr>
<td>316 SS</td>
<td>0.35</td>
<td>482</td>
<td>1849</td>
<td>325.1</td>
<td>[21]</td>
</tr>
<tr>
<td>Fe-9Cr-1Mo</td>
<td>0.35</td>
<td>482</td>
<td>1849</td>
<td>8.3</td>
<td>[25]</td>
</tr>
<tr>
<td>HT-9</td>
<td>0.35</td>
<td>482</td>
<td>1849</td>
<td>18.3</td>
<td>[25]</td>
</tr>
</tbody>
</table>

Table 2.2: Experimental conditions and results of corrosion tests in USA forced circulation loop.

A large number of corrosion tests were performed on martensitic steel 1.4914 and four types of RAFM steels MANET I, F82H, Optifer and EUROFER. The temperature varied from 480 °C to 550 °C. The liquid alloy was changed from Pb-17Li to eutectic composition. The corrosion behavior was determined by measuring the diameter on fresh and corroded samples or the width of corrosion layer under SEM. The main experimental conditions and results of corrosion tests performed in PICOLO loop are listed in Tab. 2.3.

<table>
<thead>
<tr>
<th>Liquid alloy</th>
<th>Steel</th>
<th>Velocity (m/s)</th>
<th>Test temperature (°C)</th>
<th>Exposure time (h)</th>
<th>Corrosion rate (µm/y)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-17Li</td>
<td>1.4914</td>
<td>0.3</td>
<td>550</td>
<td>3700</td>
<td>370</td>
<td>[23]</td>
</tr>
<tr>
<td>Pb-17Li</td>
<td>MANET I, F82H, Optifer</td>
<td>0.3</td>
<td>480</td>
<td>8000</td>
<td>100</td>
<td>[32,33]</td>
</tr>
<tr>
<td>Pb-17Li</td>
<td>EUROFER</td>
<td>0.3</td>
<td>480</td>
<td>12000</td>
<td>90</td>
<td>[35]</td>
</tr>
<tr>
<td>Pb-17Li</td>
<td>EUROFER</td>
<td>0.3</td>
<td>550</td>
<td>1025</td>
<td>700</td>
<td>[36]</td>
</tr>
<tr>
<td>Pb-17Li</td>
<td>EUROFER</td>
<td>0.22</td>
<td>480</td>
<td>12000</td>
<td>80</td>
<td>[38]</td>
</tr>
<tr>
<td>Pb-17Li</td>
<td>EUROFER</td>
<td>0.22</td>
<td>550</td>
<td>12000</td>
<td>400</td>
<td>[37]</td>
</tr>
<tr>
<td>Pb-15.7Li</td>
<td>EUROFER</td>
<td>0.1</td>
<td>550</td>
<td>3000</td>
<td>300</td>
<td>[38]</td>
</tr>
</tbody>
</table>

Table 2.3: Experimental conditions and results of corrosion tests in PICOLO forced circulation loop.

The corrosion rate for MANET I, F82H and Optifer exposed to flowing Pb-17Li at 480 °C and at flow of 0.3 m/s was 100 µm/y. The corrosion rate for EUROFER (reference structural material for EU TBM) tested under the same condition was 90 µm/y. As a result, among all proposed RAFM steels, EUROFER has the best corrosion resistance.

In this thesis, we focus on the corrosion behavior of EUROFER in flowing eutectic Pb-Li.
2.3 Corrosion mechanism

To study corrosion mechanism of EUROFER in liquid Pb-Li alloy, SEM/EDX analyses are applied on the tested samples. This technique can observe the surface morphology and roughness to determine corrosion attack and can investigate elements concentrations from corrosion layer to steel matrix.

Fig. 2.4 shows the EDX line scan measurements together with the corresponding SEM picture of a EUROFER sample exposed for 3011 h to Pb-17Li at 480°C and flow rate of 0.3 m/s in PICOLO loop. The path for performing the elements analyses was marked by crosses ranging from the embedding resin to the steel. Under investigation were the elements Fe, Cr, Mn, W (the main steel components) as well as Pb and O. The left part of EDX line scan was corresponding to the adherent Pb-17Li corrosion layer and the right one was EUROFER steel matrix [35].

It is observed that the concentrations of the main steel components (element Fe, Cr, W and Mn) were constant in the steel matrix. And small concentrations of steel components were detected in the corrosion layer. The
2. Corrosion behavior in eutectic Pb-Li

Figure 2.4: SEM (right) and EDX (left) analyses of EUROFER exposed to Pb-17Li for 3011 h at 480°C and flow rate of 0.3 m/s in PICOLO loop (Ref. [35]).

measured values were about 2% for Fe and Cr, 1% for W and 0.1% for Mn. The enrichment of element W was detected in the corrosion layer as well. There was no Pb detected in the steel matrix, hence there was no Pb infiltration into the steel matrix [35].

From the elements concentrations of corrosion layer and steel matrix, the most probable corrosion mechanism of EUROFER in liquid Pb-Li is dissolution mechanism. When liquid Pb-Li attacks steel surface, the steel alloying elements dissolve into liquid Pb-Li and form a Pb-Li filled porous corrosion layer. The amount dissolved at equilibrium, i.e. solubility, is an important parameter of process of dissolution. Different steel alloying elements have different solubilities in liquid Pb-Li. The steel alloying elements with relatively high solubility in liquid Pb-Li are leaching out of steel matrix very fast. The concentrations of steel components Fe and Cr were very low in the corrosion layer in Fig. 2.4 because of their high solubilities in Pb-17Li. While other elements with low solubility (e.g. W) remain in the steel matrix and even are enriched in the corrosion layer [32–37].

The microstructure of corrosion layer can be used to study surface morphology and roughness to determine corrosion attack. Fig. 2.5 shows the microstructure of the corrosion zones near a small unattacked area of EUROFER sample exposed for 500 h (left) and 1025 h (right) to Pb-17Li at 550°C and flow rate of 0.3 m/s in POCOLO loop [36]. The selected sections of the surfaces revealed an unwetted area with no adherent Pb-Li and nearby surfaces with localized corrosion attack. As a result the corrosion attack occurs locally on the steel surface and the corrosion attack is inhomogeneous and incomplete for short exposure time. In the regions with an adherent Pb-17Li layer in Fig. 2.5, corrosion attack may had started shortly after inserting the samples into the test loop due to similar corrosion attack for the time spans 0-500 h.
2.4 Effect of temperature and flow velocity

Figure 2.5: Microstructure of corrosion zones near a small unattacked area of EUROFER exposed to Pb-17Li for 500 h (left) and 1025 h (right) at 550°C and flow rate of 0.3 m/s in POCOLO loop (Ref. [36]).

and 500-1000 h. They also showed that corrosion attack proceeded linearly with exposure time [36].

It is also observed that a complete and mostly uniform corrosion attack occurs for longer exposure time. This phenomenon is called incubation effect. The most probable explanation is start of corrosion at a different time scale, i.e. delayed wetting. The microstructure found after etching suggested that the corrosion attack seemed to be stronger at formerly austenitic grain boundaries and at positions with a high density of grain boundaries. So the different microstructures on the surface of steel probably lead to corrosion attack at different time or speed and delayed wetting [34–37].

If taking unattacked areas as a zero line, the metal loss can be easily determined on the cross-sectional cuts of steel sample. However, for longer exposure time, there are no more unattacked areas, which could be used a zero line. Unfortunately, no additional marker can be set on the sample surface of original materials before exposure. Therefore, the metal loss values measured on very long time are probably too low and cannot be considered [32].

2.4 Effect of temperature and flow velocity

The corrosion rate of steel in liquid breeder is strongly dependent on temperature, flow velocity and other thermal-hydraulics conditions of testing loop.

A series of corrosion tests of EUROFER in flowing Pb-Li have been carried out in the forced circulation loop PICOLO in Germany over last ten years [35–38] listed in Tab. 2.3 in section 2.2.3. In the new HCLL blanket design the operation temperature was increased from 480°C to 550°C and the lead-lithium alloy was changed from Pb-17Li to Pb-15.7Li [38]. So the operation temperature of new test section in PICOLO loop was also increased from
480°C to 550°C. In the new HCLL blanket design the flow velocity of Pb-Li was required to be in pure laminar flow (flow rate \(\approx 1 \text{ cm/s}\)) condition [38]. However, most of the corrosion tests were performed at high flow velocities (e.g. 30 cm/s, 22 cm/s) corresponding to turbulent flow regime. A new corrosion test at reduced 10 cm/s flow velocity was also carried out recently.

It is indicated that the steel corrosion rate is strongly dependent on temperature and flow velocity. At the same flow velocity of 22 cm/s in Tab. 2.3, there is a dramatic increase of corrosion rate from 80 to 400 \(\mu\text{m/y}\) at the temperature 480°C and 550°C. For the same temperature, the corrosion rate is decreasing with decreased flow velocity.

The new corrosion test at reduced 10 cm/s flow velocity was to produce data for modeling validation which was used for reliable data extrapolation predictions to real TBM or DEMO operation condition. Due to short exposure time (only 3000 h) for reduced flow velocity and blank data for laminar flow range, longer exposure time test and further test for laminar flow range are required in the future campaigns.

The first removed sample at reduced flow velocity of 10 cm/s after 500 h showed incomplete corrosion attack similar to samples removed at flow velocity of 22 cm/s after 500 h. About 3% of the surface were not or delayed wetted. This means, also at reduced flow velocity incubation effects occur, however, the period is in the order of the 550°C tests performed at 22 cm/s and not comparable with incubation period determined at 480°C near 1200 h [37,38]. This may indicate that incubation effects are more sensitive to temperature than to flow velocity in the turbulent regime.

Fig. 2.6 shows the metal loss as function of temperature and flow velocity by using MATLIM code with Sannier’s correlation. Computational code MATLIM [39] is developed to calculate the mass transfer in liquid metal loops based on dissolution mechanism discussed in section 2.3. It is also indicated that the steel corrosion rate is dependent on temperature and flow velocity. For the required temperature, reducing the liquid flow velocity is a very good way to decrease the corrosion rate.

The experimental data are compared with the corrosion curves for flow velocity of 22, 5 and 0.5 cm/s. The corrosion values evaluated at 480 and 550°C in PICOLO loop are slightly below the empirical line but with the same temperature dependency. The value for the newly started 10 cm/s campaign lies clearly below the 22 cm/s value and above predictions for the 5 cm/s range. This is an indication that the extrapolated value with poor data base at only short exposure times will guide to reliable values. However, it has to be pointed out that long term exposure data points are absolutely necessary. Without them the validation of MATLIM or other correlations will be not resilient [38].
2.5 Effect of magnetic field

Fusion reactor is a magnetic confinement machine, so the materials will suffer from a strong magnetic field and the research of the effect of magnetic field on the corrosion processes is necessary. That’s because of the change of hydrodynamics of liquid metal flow, and because of interaction of a magnetic field with a ferromagnetic steel.

Most of the corrosion tests having been done over last thirty years are without magnetic field. However, the research of the effect of magnetic field on the corrosion processes is ongoing recently.

With the support of EFDA Technology Workprogramm, a long-term experimental Pb-17Li loop in a magnetic field was designed and built in University of Latvia [40, 41]. The principal schematic of experimental setup is shown in Fig. 2.7. The main units of the facility were following: a loop assembly, an electromagnet, an EM induction pump with permanent magnets, an EM conductive flow meter, a heat exchanger, a cold trap, an expansion tank, a supply container, a test section and heaters. The loops consisted of two parts: a cold part and a hot part. In the cold part of the loop (behind the heat exchanger, at the inlet of the cold trap, in the EM flow meter and in the pump), the temperature was kept within the range of 350-400°C. The operating temperature
2. Corrosion behavior in eutectic Pb-Li

Figure 2.7: Principal schematic of Pb-17Li loop for EUROFER corrosion experiments in a magnetic field. 1 – test section; 2 – liquid metal loop; 3 – level meter; 4 – expansion tank; 5 – heater; 6 – cold trap; 7 – flow adjusting valve; 8 – heat exchanger; 9 – expansion tank; 10 – EM flow meter; 11 – supply container; 12 – vacuum meter; 13 – vacuum pump; 14 – argon balloon; 15 – magnet pole shoes; 16 – device for adjusting oil level in the heat exchanger; 17 – oil supply tank. (Ref. [40]).

in the test section was 550°C and the maximum intensity of the magnetic field in the area of test section was 1.7 T.

Fig. 2.8 shows the schematics of test section and sample in detail. The test section included a removable part as long as 600 mm with samples mounted inside and an input section as long as 500 mm for driving a developed melt flow. The inner rectangular cross-section (10 × 27 mm²) along the entire length of the test section was uniform. The outer frame of the test section, also having a rectangular cross-section, was formed by pressing of a round tube with the inner inlet diameter D = 27.3 mm and wall thickness of 1.5 mm. The height of the channel (inner dimension in the direction of magnetic field) was chosen 13 mm. The removable part of the test section was divided into three zones. In the first and third zones the entire inner surface of the channel was plated with EUROFER samples at a maximum distance from magnet poles in the region of the scattered magnetic field. To eliminate the influence of this relatively weak scattered field on the flow, this zone had a ferromagnetic screen. The third zone (120 mm long) was located in the gap between the magnetic poles.
2.5 Effect of magnetic field

Figure 2.8: schematics of test section and sample in detail (Ref. [40]).

and started inside the gap at a distance of about one width of the channel in the region, where magnetic field was already uniform.

Ten EUROFER samples (Nr.1-10, direction of flow from Nr.1 to Nr.10) were L-shaped plates as thick as 1.5 mm as wide as 12 mm plated continuous inside the rectangular test section with nearly uniform magnetic field or without magnetic field. The samples were adjusted close each to other, so allowing minimal penetration of the liquid melt between them.

Three experiments were carried out with different conditions listed in Tab. 2.4. The testing time was 2000 h for each experiment. Due to some technical reasons, the experiment was twice interrupted for a short time during first session of experiments.

<table>
<thead>
<tr>
<th>Test session</th>
<th>magnetic field in the gap (T)</th>
<th>Test temperature (°C)</th>
<th>Min. temperature in the loop (°C)</th>
<th>Velocity of melt in test section (cm/s)</th>
<th>Layout of samples against magnetic field</th>
</tr>
</thead>
<tbody>
<tr>
<td>First session</td>
<td>1.7</td>
<td>550-570</td>
<td>350</td>
<td>5</td>
<td>Long wall perpendicular to magnetic field</td>
</tr>
<tr>
<td>Second session</td>
<td>1.7</td>
<td>550-560</td>
<td>350</td>
<td>2.5</td>
<td>Long wall perpendicular to magnetic field</td>
</tr>
<tr>
<td>Third session</td>
<td>1.5</td>
<td>550-560</td>
<td>350</td>
<td>5</td>
<td>Long wall parallel to magnetic field</td>
</tr>
</tbody>
</table>

Table 2.4: Conditions of three sessions of corrosion experiment (Ref. [40]).
Upon completion of each experimental session, the tested samples were removed from the test section and some of them were cleaned off the residue of the corrosion medium by holding additionally in lithium under static conditions at 400 °C during 2-2.5 hours then were washed off lithium in ethanol and further in distilled water.

For the second session, new L-shaped samples were arranged in the Test Section, except samples Nr.9, instead of them equivalent not washed samples already been exposed during first session. For the third session, all new samples were used.

The results of gravimetric analysis illustrated the phenomena associated with the location of the samples. It was found that the value of sample mass loss or steel dissolution rate decreased from sample Nr.1 to Nr.5 (the flow direction) and was more or less the same from Nr.6 to Nr.10. A probable explanation is the saturation of a liquid metal solution with steel components and, due to this, the decay of the dissolution motive force. Magnetic field enhanced corrosion was observed that the total mass loss of all samples located in magnetic field was about twice large compared to values for samples without magnetic field.

![Figure 2.9: Corrosion rate for three experimental sessions with and without magnetic field (Ref. [40]).](image)

Corrosion rate was identified by sample mass change with correction of dissolution kinetics of steel surface layer and also temperature conditions. Fig. 2.9
2.5 Effect of magnetic field shows the comparison of corrosion rate for three experimental sessions with and without magnetic field. In general, the imposition of a magnetic field had enhanced the intensity of corrosion processes more than twice compared to condition without magnetic field. The decrease of liquid flow velocity in twice (flow velocity decreased from 5 cm/s to 2.5 cm/s) had resulted in the corrosion rate decrease by 26% on the average. The change of the test section orientation about the magnetic field direction at least had not decreased the corrosion intensity.

![Macrostructure of washed EUROFER sample surfaces with (a) and without (b) magnetic field (Ref. [40]).](image)

Figure 2.10: Macrostructure of washed EUROFER sample surfaces with (a) and without (b) magnetic field (Ref. [40]).

The most interesting phenomenon which not occurred before in experiments without magnetic field is that the corrosion surfaces exposed to the magnetic field displayed ordered wave-like furrow structures oriented in the liquid flow direction whereas the surfaces were relatively smooth enough without magnetic field. Fig. 2.10 shows macrostructure of washed EUROFER sample surfaces with and without magnetic field. These furrow structures were observed only on the Hartmann (perpendicular to the magnetic field) surfaces. This is also confirmed in the third experimental session that the walls parallel to the magnetic field were smooth.

As the size of samples was small, standard tensile tests could not be performed. Mechanical properties were investigated by Brinell and Vickers hardness methods. No significant changes of hardness values were observed for the samples with magnetic field. It seems that the Brinell hardness is unaffected by the corrosion processes in magnetic field. However, hardness is not a good
parameter to evaluate the corrosion damage. As a result, it is necessary that more tests like tensile and fracture toughness tests are performed to study the effect of magnetic field on mechanical properties in the future.

2.6 Improvement proposals

The precipitates from dissolved steel components will crystallize in cooler system sections or in areas with magnetic fields and lead to a high risk of tube blockages. To reduce this risk, the corrosion rate should be decreased as much as possible.

One possible way is the reduction of Pb-Li flow rate from turbulent or mixed mode to pure laminar flow as we discussed in section 2.4.

Another improvement proposal is the coatings of structural materials with corrosion barriers. On the basis of long-term candidate materials screening, current R&D activities on coatings are mainly focused on alumina (Al₂O₃)/FeAl and erbium oxide (Er₂O₃) coatings.

![Figure 2.11: Line scan (left) and scan path (right) of EUROFER sample exposed to Pb-17Li for 6292 h at 480°C in PICOLO loop (Ref. [36]).](image)

Various methods have been used to fabricate Al₂O₃/FeAl coatings. First activities were started at Karlsruhe Research Center (FZK) roughly one decade ago. At that time a coating technique based on dipping of the work pieces into an Al-melt and subsequent heat treatment was developed. This technique was called Hot-Dip Aluminization (HAD). Fig. 2.11 shows the surface of EUROFER sample exposed to Pb-17Li for 6292 h at 480 °C in PICOLO loop and the line scan performed along the marked path in the SEM picture. The highest Al level was about 50 wt% in the near surface region which was in contact with the Pb-17Li melt and belonged to the phase FeAl₂ with a thickness of about 20 µm. The FeAl₂ field was followed by the next stable phase FeAl.
2.6 Improvement proposals

Between FeAl and the EUROFER matrix, a continual Al decrease in the $\alpha$-Fe was visible. The Al reacted zone was roughly 120 $\mu$m thick. The three Al phases detected in the line scan could be correlated to the different grey colors in the SEM picture shown on the left. The microstructure indicated that the Al-rich phase FeAl$_2$ was strongly attacked and partially removed as can be seen in the lower part of the picture. It seemed that the corrosion attack was delayed or stopped after reaching the FeAl phase [36].

However, HAD technique has great difficulty in controlling the homogeneity or thickness of the Al scale and removing excessive Al. A recently developed electro-chemically-based coating technique can overcome those drawbacks. Electro-Chemical Al (ECA) technique is based on the electro deposition of aluminum from an organic electrolyte where Al is existing as an Al(C$_x$H$_y$) complex. Using this technique, at least two main criteria – homogeneous coating structure and reduction of deposited Al amount are fulfilled. Additionally, the formation of corrosion resistant phases and surface quality (pores, roughness) rely on proper heat treatment parameters and gas atmosphere conditions. During this process, Al reacts with the steel and forms an Al-riched zone with a thin protective Al$_2$O$_3$ surface scale [42]. The form of ductile $\alpha$-Fe(Al) phase layer on the surface of steel has good corrosion resistance which is confirmed in the experimental tests [36,42–44].

![Figure 2.12: Micrograph of an ECA coated cylindrical EUROFER sample exposed to Pb-15.7Li for 5298 h at 550°C and flow velocity of 0.22 m/s in PICOLO loop (Ref. [43]).](image)
Fig. 2.12 shows the micrograph of an ECA coated cylindrical EUROFER sample exposed to Pb-15.7Li for 5298 h at 550°C and flow velocity of 0.22 m/s in PICOLO loop. Clearly visible is the EUROFER matrix, the α-Fe(Al) grains (roughly 40-50 µm in radial dimension) together with Kirkendall pores (5-10 µm) and the adherent Pb-15.7Li scale. It is clearly showed that no corrosion attack is visible in a material taken of below the Kirkendall pores during this test. As comparison bare EUROFER samples under the same testing conditions suffered a material loss of about 400 µm/y or for the testing time 5300h roughly 240 µm erosion. It can be concluded that Al coating samples have surely a protective surface scale which acted as corrosion barrier [43].

There are other possible methods to fabricate Al₂O₃/FeAl coatings such as chemical vapor deposition (CVD) [45], atmospheric/low pressure/vacuum plasma spray (APS/LPPS/VPS) method [46,47], sol-gel method [48] or Al-pack cementation [49] which are not discussed in detail here.

For Er₂O₃ coatings, several fabrication methods are developed, including filtered arc deposition [50], magnetron sputtering [51], metal-organic decomposition [52], sol-gel method [53], etc. A compatibility study of Er₂O₃ and Er₂O₃-Fe two-layer coatings on RAFM steel F82H with lithium-lead alloy was recently carried out in Japan. The Er₂O₃ coatings were fabricated by filtered arc deposition and then Fe coatings were deposited on some Er₂O₃ coatings by radio-frequency magnetron sputtering. The static Pb-15.7Li immersion experiments at 400-600°C for 100, 500 and 1505 h were performed. Both Er₂O₃ and Er₂O₃-Fe two-layer coatings showed good corrosion resistance compared to bare steel in liquid lithium-lead alloy. Furthermore, the outer Fe layer played a role to decrease corrosion rate of the coatings by comparing with the results of Er₂O₃ single layer coatings [54].

New activities are also testing tungsten-based scales as corrosion barriers including sandwich coatings of Al₂O₃ or Er₂O₃ together with W [55].
Chapter 3
Corrosion behavior in ceramics

The use of solid ceramic breeders, despite its relatively low thermal conductivity, presents several advantages. Among them is low chemical activity, which is important to get a good compatibility with the structural materials and coolant [56]. The study of corrosion susceptibility for solid ceramic breeders is limited so far. Although it is expected that the corrosion degradation caused by solids is much lower than that due to liquid, it is still not negligible and should be evaluated properly.

This chapter starts from general concepts of solid state reaction and steel oxidation mechanism. Afterward it collects recent published research results. At last it discusses the experimental details and results of corrosion tests carried out at Ciemat, Spain.

3.1 Corrosion mechanism

The reaction between steels and solid ceramic breeders is difficult to occur. However this process is still happened at the interfaces with a slow reaction rate. The main corrosion mechanism is the oxidation mechanism of steels due to ceramic pebbles containing oxygen.

3.1.1 Solid state reaction

Solid state reaction is the chemical reaction in which solid reacts with other substance, particularly referring to solid-solid reaction. The simplest reaction model is shown in Fig. 3.1. The chemical reaction of reactants A and B occurs at the interface and a product layer C is formed which separates the reactants. As a result subsequent reaction requires mass transport through the product layer. Ions from A and B have to counter-diffuse through product layer to form new product at the interfaces A/C and B/C [57].

The reaction rate between two solids depends on the contact area between reactants, the rate of nucleation and the rate of ions diffusion. Ions in solids are not mobile at low temperatures so that the mass diffusion rate and reaction rate will be very slow at low temperatures. For high temperatures, the diffusion
3. Corrosion behavior in ceramics

3.1.2 Oxidation mechanism of steels

Oxidation reaction of steels will occur at the surfaces of steels and lithium ceramic pebbles (Li$_4$SiO$_4$, Li$_2$TiO$_3$, Li$_2$O, etc.) contained oxygen when steels contact with these lithium ceramics. In this case, the product layer is called oxide film.

Numerous mechanisms of reaction have been considered to account for the many temperature-dependent oxidation phenomena observed. The many models differ in their assumptions about the rate-determining process: the transport mechanism through the oxide film, the driving forces of these transport mechanisms, etc. In general, for a particular metal the oxidation mechanism will be a function of surface characteristics of the sample, temperature, elapsed time of reaction. When the large variations of the properties of different metals and their oxides are also considered, it is not surprising that a large number of theories and models have been put forward to explain the kinetics of oxidation of metals. The steels contain different alloying elements whose electrochemical potential in a specific environment will determine the nature of oxide layer.

Corrosion rate equations which are commonly encountered are commonly classified as logarithmic, parabolic and linear. They represent only limiting and ideal cases. Deviations and intermediate rate equations are often encountered.
3.2 Previous study review

Direct logarithmic:

\[ x = k_{\text{log}} \log(t + t_0) + A \]  

(3.1)

Inverse logarithmic:

\[ 1/x = B - k_{\text{il}} \log t \]  

(3.2)

where \( x \) represents the thickness of the oxide film or mass change of steels, \( t \) denotes the time, \( k_{\text{log}} \) and \( k_{\text{il}} \) represent the rate constant, and \( A \) and \( B \) are integration constants;

Parabolic:

\[ x^2 = k_p t + C \]  

(3.3)

where \( k_p \) represents the parabolic rate constant;

Linear:

\[ x = k_l t + D \]  

(3.4)

where \( k_l \) represents the linear rate constant.

In many cases it is difficult or even impossible to fit rate data to simple rate equations. Oxidation reactions are frequently found to follow a combination of rate laws [58].

3.2 Previous study review

Not so much study about compatibility issue of structural materials with lithium ceramics have been done so far. The published literature is very limited.

A compatibility test of ceramic solid breeders (\( \text{Li}_2\text{O}, \gamma\text{-}\text{LiAlO}_2 \) and \( \text{Li}_2\text{SiO}_3 \)) with candidate structural materials (Type 316 stainless steel, HT-9, Inconel-625 and Ti-6242) was done at 600°C in a pure helium (99.99%) atmosphere for 1900 h in USA early in 1981.

The configuration of the ceramic/alloy couples in the sample holder (type 304 stainless steel) is shown in Fig. 3.2. The tip of the chromel/alumel thermocouple attached to the outer cover of the sample holder was located parallel to and in the middle of the sample section.

After test, the ceramic plates were examined using powder X-ray diffraction. Scanning electron micrographs (SEM) and X-ray maps were made of the ceramic plates as well. The corrosion scale formation was greatest for \( \text{Li}_2\text{O}/\text{alloy} \) couples typically >15 \( \mu \)m thick. The scales on \( \text{Li}_2\text{SiO}_3/\text{alloy} \) and on \( \gamma\text{-LiAlO}_2/\text{alloy} \) were comparable. Some lithium oxides containing steel alloying element (\( \text{Li}_5\text{FeO}_4, \text{LiCrO}_2 \)) were detected in the corrosion scale [59].

Another simple capsule compatibility tests of three lithium-containing ceramic breeder materials \( \text{Li}_4\text{SiO}_4, \text{Li}_2\text{ZrO}_3 \) and \( \text{LiAlO}_2 \) with two industrially available SiC/SiC composites were carried out at 600 and 800°C under two testing conditions (flowing helium and dynamic vacuum) for 1000 h in Italy in 1994. The schematic diagram of the apparatus is shown in Fig. 3.3. After
3. Corrosion behavior in ceramics

Figure 3.2: Experimental configuration showing the sample stacking order within the sample holder (Ref. [59]).

tests, analyses of SEM micrographs and glancing angle X-ray diffraction were performed on the surfaces of SiC/SiC composites.

All three breeder materials were reactive towards the SiO\(_2\) content of the SiC/SiC composites forming a surface layer of Li\(_2\)SiO\(_3\) in flowing helium:

\[
Li_4SiO_4 + SiO_2 \rightarrow 2Li_2SiO_3 \tag{3.5}
\]

\[
Li_2ZrO_3 + SiO_2 \rightarrow Li_2SiO_3 + ZrO_2 \tag{3.6}
\]

\[
2LiAlO_2 + SiO_2 \rightarrow Li_2SiO_3 + Al_2O_3 \tag{3.7}
\]

The Li\(_2\)SiO\(_3\) layer was thickest produced by Li\(_4\)SiO\(_4\) breeder because initially evolved CO\(_2\) produced from thermal decomposition of Li\(_2\)CO\(_3\) impurity in Li\(_4\)SiO\(_4\) breeder would oxidize the SiC/SiC composites surface to form SiO\(_2\). The layer became thinner in the dynamic vacuum condition due to greater efficiency of removal of gaseous impurities, originating from outgasing or de-
3.2 Previous study review

Figure 3.3: Schematic diagram of the apparatus: (1) molybdenum crucible; (2) SiC/SiC composites; (3) ceramic breeder material; (4) furnace; (5) helium bottle; (6) vacuum gauge; (7) reaction chamber; (8) heated tube; (9) vacuum chamber; (10) mass spectrometer; (11) recorder; (12) UHV system; (13) thermocouple (Ref. [60]).

composition of impurities from the breeder materials to prevent oxidation of SiC to SiO$_2$ [60].

For RAFM steels, there are some groups working in EFDA Technology Workprogramme to study interaction chemistry between EUROFER structural material and lithium ceramic pebbles. However the results of their work are under confidential that cannot be reviewed in this thesis.

The only published literature (Ref. [56]) is from lithium ceramics point of view to study their chemical compatibility with EUROFER samples. The EUROFER samples were placed inside a lithium ceramic pebble bed (Li$_2$TiO$_3$, Li$_4$SiO$_4$) at 600 $^\circ$C under a reducing atmosphere obtained by the flow of a purge gas composed of He + 0.1vol.% H$_2$ for exposure time from 50 to 2000 h [56].

The lithium ceramic pebbles analyzed for each exposure periods were divided in two subsets: one containing pebbles forming the pebble bed and the other one containing pebbles that were directly removed from the surface of the EUROFER samples. Ion beam nuclear microprobe techniques with Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS) analyses were used for the characterization.

For the lithium orthosilicate pebbles, PIXE spectra obtained from pebbles
Figure 3.4: (First and second row) SEI, Si and Fe maps obtained from the lithium orthosilicate pebbles for 50 h exposure time (first row – pebbles in the pebble bed; second row – pebbles in close contact with EUROFER). (Third row) Si, Fe and Cr elemental maps of a lithium orthosilicate pebble in close contact with EUROFER for 200 h exposure time (Ref. [56]).

in the pebble bed showed appearance of EUROFER alloying elements such as S, Ti and Fe. Furthermore, the pebbles in close contact with EUROFER presented PIXE spectra with a much wider variation on those elements. As an example, Fig. 3.4 shows the secondary electron images (SEI) and some elemental maps obtained from pebbles in the pebble bed and in close contact with the EUROFER sample. For the same exposure time of 50 h (first and second row), there was an increase in Fe content for pebbles in close contact with EUROFER. This seemed to be due to a localized contamination from EUROFER steel. In the third row, the Cr and Fe contaminations did not have the same spatial distribution. This was in accordance with the expected formation of Fe and Cr oxides. As a result lithium orthosilicate pebbles were contaminated by EUROFER steel and there were chemical reactions to form
different types of compounds.

For lithium metatitanate pebbles, the contamination from EUROFER elements was not found. Apart from an increase in the irregularities of the pebble surface, chemical composition alterations that could justify the pebble color change from white to blue above 500 h of exposure time were not found. This could be an indication that the coloration was related with phase transformation, including the formation of different Ti oxides [56].

3.3 Experiments at Ciemat

3.3.1 Experimental setup and procedure

The experimental setup mainly consisted of a horizontal cylindrical oven, purge gas system, a tubular 316 L stainless steel capsule. The schematic of this setup is shown in Fig. 3.5.

The chemical compatibility tests of four types of RAFM steels (EUROFER, F82H, ODS EUROFER and PM2000) in lithium orthosilicate pebble bed were carried out at 550°C (the reference working temperature in steels in EU HCPB
TBM design [8]) for testing periods of 1, 2, 4 and 8 weeks. In the following discussion, we only focus on the corrosion behavior of EUROFER in lithium orthosilicate.

The first experimental step is materials preparation. The ceramic pebbles of lithium orthosilicate were obtained at Ciemat laboratory of material by spray-drying technique followed by pyrolysis. The raw materials were the stoichiometric amounts of lithium acetate and silicon tetraacetate respectively of analytical grade. After drying, the powder obtained was heating at 600°C to reach the crystalline lithium orthosilicate phase and preserve the adequate spherical shape [61]. The samples of EUROFER with chemical composition (wt%) 0.1C, 9Cr, 1W, 0.12Ta, 0.23V, 0.5Mn, 0.001S, balance Fe were cut into rectangular pieces and grinding up to 600 SiC paper-grit (equivalent to 26 µm roughness approximately) with final dimensions of 20×15×8 mm³. Before testing, the samples were cleaned in ultrasonic ethanol bath, dried and weighted.

The second step is main test. All the RAFM steel samples (two for each type) were hung to a rod as in Fig. 3.6(a) and the rod was inserted into the stainless steel capsule. The capsule was filled with lithium orthosilicate powder and connected to a mixed purge gas of He/0.1% H₂ (the composition of purge gas in EU HCPB TBM design [8]) at 1 MPa. The working temperature of the oven was set as 550°C. The testing periods were 1, 2, 4 and 8 weeks.

![Samples of RAFM steels](image)

Figure 3.6: Samples of RAFM steels (a) before testing, (b) after testing for 4 weeks.

After finishing the test and temperature of oven decreased to room temperature, the tested samples were taken out from the capsule shown in Fig. 3.6(b). All the samples were cleaned in ethanol, measured and weighted. Then sample
preparations of cutting, mounting, grinding and polishing were done to steel cross section.

The final step is characterization of tested samples. Metallographic studies were performed in cross section for all samples by SEM/EDX analyses (JEOL Mod. JSM 6400 EDX) and Superprobe JXA-8900 M equipped with an Electron Probe Micro Analyzer (EPMA). The corrosion products were determined by X-ray diffraction (XRD, PAnalytical Mod. X’Pert PRO MRD).

\subsection*{3.3.2 Results and discussions}

After exposure, the surface color of EUROFER sample changed from metallic to dark as shown in Fig. 3.6. That means there is chemical reaction occurring on the steel surface.

The mass change measurements are not accurate because surface descaling occurs during cleaning. The approximate mass change of EUROFER samples with time is corresponded to a logarithmic law.

Fig. 3.7 shows the SEM/EDX analyses results of cross section of EUROFER sample surface for the exposure time of 1, 2, 4 and 8 weeks. The corrosion layer was observed to be uniform all over the surface and thick of about 18-25 $\mu$m.

From all the SEM images, the corrosion layer was mainly formed by two layers containing oxygen which is corresponding to oxides layer. The nearest layer to the base material was compact. It was depleted in Fe and enriched in Cr compared to the steel matrix. In contrast, the outer layer was very porous and exhibited lower density. The concentration of Fe was decreased comparing to the steel matrix while increased comparing to the inner corrosion layer. The concentration of Cr became almost negligible in this layer.

A visible gap was found between base material and oxidation layer at the SEM images of the samples for the exposure time of 2, 4 and 8 weeks. The possible reason is that corrosion layer became a little detached from the base material during sample preparation.
Figure 3.7: SEM/EDX analyses results of cross section of EUROFER sample surface for the exposure time of 1, 2, 4 and 8 weeks.
Chapter 4

Conclusions

4.1 Conclusions

4.1.1 Corrosion behavior in eutectic Pb-Li

1. The lithium concentration of eutectic Pb-Li is 15.7 at%.
2. Corrosion mechanism is dissolution of steel alloying elements into liquid Pb-Li.
3. Corrosion rate is dependent on temperature, flow velocity and magnetic field. The lower temperature, the lower corrosion rate. The lower velocity, the lower corrosion rate. The magnetic field enhances the corrosion rate and forms furrow structure on the steel surface that may change the mechanical properties.
4. Application of corrosion resistant coatings on the structural materials is a possible way to significantly reduce the corrosion rate.

4.1.2 Corrosion behavior in ceramics

1. The corrosion mechanism is based on solid reaction and oxidation of steel. However, this mechanism is very complex and needs to be studied clearly.
2. The analyses of lithium ceramic pebbles show the contamination of steel alloying elements on the surface. Different spatial distributions of alloying elements are in accordance with the expected formation of oxidation products.
3. After the corrosion tests carried out at Ciemat, the surface color of EUROFER sample changes from metallic to dark. The mass change with time is corresponded to a logarithmic law.
4. The analyses of tested EUROFER sample show the formation of two oxidation layers with different morphology on the surface.

4.2 Future work

1. The previous tested steel samples were too small to perform test of mechanical properties (e.g. tensile test, fracture toughness test). In order
to determine how serious this corrosion behavior affect the steel mechanical properties, related tests need to be performed.

2. The corrosion tests of proposed structural materials in eutectic Pb-Li of reduced flow regime (flow velocity < 10 cm/s) need to be carried out towards TBM design.

3. The corrosion tests of proposed structural materials in lithium ceramics need to be carried out with more exposure time. The corrosion mechanism needs to be studied more clearly.

4. The effect of surface contamination of ceramic pebbles on materials properties (e.g. thermo-mechanical properties, tritium release) needs to be studied.
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Declaration in lieu of oath

Herewith I declare in lieu of oath that I have prepared this thesis exclusively with the help of my scientific teachers and the means quoted by them.

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