Corrosion of some candidate structural materials for lead fast reactors

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Abstract Among the six types of reactors of great importance for Generation IV, at European level, is the Lead Fast Reactor (LFR). The most challenging aspect of lead-based technology is the corrosive nature of this liquid metal that requires careful oxygen control and the use of structural materials with high corrosion resistance. The purpose of this paper is to present the structural materials of the main equipment from a LFR and to describe the processes related to their degradation. The paper contains experimental results obtained through the exposure of structural materials in the presence of liquid lead. After testing, the materials were analysed by visual examination, optical microscopy and microhardness determinations. The paper also presents new research directions to be approached in order to know in detail the processes that occur when the metallic materials come into contact with liquid lead.

Keywords: structural materials, LFR, corrosion, Oxygen Concentration System (OCS).

1. Introduction

The enormous potential of nuclear power as an attractive option in terms of security of supply and global climate change is more and more recognized by energy policy makers, industry leaders and technical experts. Therefore, nuclear

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energy is expected to play a key role in meeting increased energy demand across the world.

Following the Fukushima accident, in March 2011, there has been a strong need for a safer nuclear power and the consequence of this is the intensification of research regarding the Generation IV reactors. These types of reactors have the advantage of being sustainable, economical, reliable and safe due to the reduced probability of core degradation by eliminating any need for off-site emergency intervention.

The objectives adopted by the GIF (Generation IV International Forum) involve a sustained activity to identify and select six nuclear power systems for further development. The selected systems are based on a technological diversity of reactors, energy conversion modes and closed or open fuel cycles. The types of thermal neutron reactors or fast neutron reactors, the closed or open fuel cycles as well as a wide range of reactor capacities from very small to very large reactors are all research directions.

Depending on the degree of technical maturity of Generation IV systems, they are expected to be commercially available from 2030 onwards.

All Generation IV systems aim to improve performance, new applications in nuclear power and/or sustainable approaches to nuclear material management. High temperature systems offer the possibility of applying both to efficient energy processes and (possibly) hydrogen production. Improving sustainability is mainly achieved through the adoption of a closed fuel cycle including the reprocessing and recycling of plutonium, uranium and secondary actinides in fast neutron reactors and also through high thermal efficiency. This approach ensures a significant reduction in the amount of waste generated and the uranium resource needs, [1].

Table 1 shows the main features of Generation IV systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Neutron spectrum</th>
<th>Coolant</th>
<th>Temp. (°C)</th>
<th>Fuel cycle</th>
<th>Size (MW_e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHTR (Very High Temperature Reactor)</td>
<td>thermal</td>
<td>helium</td>
<td>900-1000</td>
<td>open</td>
<td>250-300</td>
</tr>
<tr>
<td>SFR (Sodium-cooled Fast Reactor)</td>
<td>fast</td>
<td>sodium</td>
<td>550</td>
<td>closed</td>
<td>30-150 300-1500 1000-2000</td>
</tr>
<tr>
<td>SCWR (Super-Critical Water-cooled Reactor)</td>
<td>thermal / fast</td>
<td>water</td>
<td>510-625</td>
<td>open/closed</td>
<td>300-700 1000-1500</td>
</tr>
<tr>
<td>GFR (Gas-cooled fast Reactor)</td>
<td>fast</td>
<td>helium</td>
<td>850</td>
<td>closed</td>
<td>1200</td>
</tr>
<tr>
<td>LFR (Lead-cooled Fast Reactor)</td>
<td>fast</td>
<td>lead</td>
<td>480-800</td>
<td>closed</td>
<td>20-180 300-1200 600-1000</td>
</tr>
<tr>
<td>MSR (Molten Salt Reactor)</td>
<td>fast/thermal</td>
<td>fluoride salts</td>
<td>700-800</td>
<td>closed</td>
<td>1000</td>
</tr>
</tbody>
</table>
In Fig. 1 is schematically shown the diagram of the main components of the LFR, [2].

![Diagram of the main components of the LFR](image)

**Fig. 1.** Lead-cooled Fast Reactor (LFR) [2]

The safe and economical operation of any nuclear power system relies to a great extent, on the success of the materials of construction. Materials degradation in a nuclear power plant is extremely complex due to the various materials, environmental conditions, and stress states.

The corrosion of metals or alloys used in the construction of the equipment working in the presence of liquid metals is mainly due to the dissolution of various constituent elements of metals or alloys by the liquid metal. The way in which dissolution occurs produces different types of attack from a simple attack and reaches an intense intergranular attack with the preferential removal of an alloy constituent, [3] ÷ [40].

Given the intent of RATEN ICN to host the Advanced Lead Fast Reactor Demonstrator (ALFRED), important steps have been taken both in the organizational plan and in the research activity. At the RATEN ICN there is a special research program dedicated to this type of reactors and a significant part of this program is dedicated to the theoretical and experimental study of LFR reactor structural materials.

**LFR Structural Materials** Of all the metallic materials known to date, the ferito/martensitic steel (T91) and the austenitic stainless steels (316L and 15-15 Ti) have been selected as the main candidate structural materials for components of an LFR reactor, Table 2.
Corrosion behavior of LFR materials

The corrosive attack of solid metals can be classified into the following categories:

1. simple dissolution;
2. alloying between liquid metal and solid metal;
3. intergranular attack;
4. reaction with impurities;
5. mass transfer determined by the temperature gradient;
6. mass transfer due to the concentration gradient or the coexistence of two different metals in the liquid metal.

Corrosion in liquid metals can be influenced by many factors among which the most important are:

- temperature;
- temperature gradient;
- cyclic temperature change;
- ratio of surface area to volume;
- purity of liquid metal;
- flow rate or Reynolds criterion;
- the state of the surface of the structural material of the process equipment;
- the number of structural materials in contact with the same liquid metal;
- the properties of the structural material such as: the presence of precipitates at the grain boundary, the presence of a secondary phase, the tension’s degree of the material and the grain.

Temperature is one of the most important factors due to the fact that a higher temperature results in a higher solubility of the solid metal in the liquid metal. Also, if the temperature increases, the diffusion rate increases, which is especially important in many corrosion types that occur in liquid metals.

When there is a temperature gradient in a system involving the presence of liquid metal, the solubility difference of metal dissolved in the liquid metal, between the cold and the hot part of the system, determines the mass transfer, Fig. 2.

The cyclic change of temperature is a useful factor for explaining the erroneous results obtained in static corrosion tests when, although the test conditions are isothermal, in a facility with non-rigid temperature control, it can fluctuate appreciably around an average value. Thus, at high temperature, the solid metal passes into the metallic solution (the liquid metal) and then, when the temperature decreases, the solid metal leaves the liquid metal and precipitates inside it forming dendrites or developing a uniform layer on the surface of the structural material.

For example, the corrosion rate for the system Cu-Bi at 500°C±5°C is several times higher than at the temperature of 500°C±0.5°C.
1. Dissolution  2. Nucleation
3. Diffusion    4. Cristales transport
5. Transport of dissolved metal  6. Crystal growth and sintering (formation of deposits that can fill the flow section)

Fig. 2. The influence of thermal gradient on mass transfer [29]

The ratio between the surface area of the material and the volume of the liquid metal is a corrosion control factor under static conditions since the metal will corrode until it saturates the molten metal at operating temperature, so if the surface/volume ratio decreases, the corrosion rate will increase.

The purity of liquid metal can influence the rapidity of reaching the solubility limit and can significantly affect the tendency to wet the solid metal material by the liquid metal.

The flow rate (Reynolds criterion) is an important parameter only in loops with forced circulation provided by pumps where the laminar boundary layer thickness decreases in both the hot and the cold side of the plant when the flowrate is high. Thus, when the metal atoms move from the hot to the cold side, the diffusion length is smaller between these two regions.

The surface state is not as important as the films formed on their surface. Once the chemical balance between the liquid metal and the solid metal is reached, the surface state is no longer important, its main effect being to change the metal saturation rate. The larger the surface area exposed, the faster the metallic fluid is saturated.

When two or more solid metals are in contact, the transfer phenomenon between different metals or the mass transfer due to the concentration gradient should be considered even if the temperature is constant. In a multi-component or multiphase system, equilibrium is reached only when the chemical potential of each component in any of the phases is equal to its chemical potential in each of the other phases. A redistribution of the components between the phases of the system will take place until the equality of the chemical potentials is reached. Thus, the driving force of these processes will exist up to the equalization of chemical potentials, which results in a decrease in the free energy of the system.

The state of the material, such as grain size and other variables, should be considered due to different wetting properties of individual grains and grain
boundaries. A continuous network of carbides or oxides at the grain boundary can significantly increase the corrosion.

In all corrosion tests realised in liquid metals, these variables must be considered and controlled in the purpose of obtaining useful information with the goal of the understanding of the compatibility of structural materials with liquid metals in different processes.

Regarding the corrosion of solid materials exposed in liquid metals it can be said that this process has been observed since the beginning of the metalworking process when the handling and storage of the molten metals was imposed. Studies of this phenomenon are required when liquid metals are used in areas requiring certain physical and chemical properties.

Liquid metals can be used as reducing agents in metal production processes, and due to their excellent thermal transfer properties, they are intended to be used as cooling agents in different energy generation systems.

Processes that occur at the alloy/liquid metal interface
Corrosion in liquid metals is manifested in different ways. In the most general case, to classify the relevant corrosion phenomenon, the following processes are used:

- dissolution;
- impurities and interstitial reactions;
- alloying;
- reduction of compounds.

All these reactions involve the wetting of the structural material by the liquid metal. This phenomenon may be an inherent problem in most systems or where a solid material, which could normally be wetted by the liquid metal, has a layer that prevents wetting on the surface.

Dissolution The simplest corrosion reaction that can take place in a liquid metal is the (direct) selective dissolution. This dissolution consists in removing the atoms in the metallic material from which the equipment is built and transferring it to the liquid metal (melt) in the absence of the effects of any impurity. Such a reaction is a simple process that takes place in the solution and for this reason is determined by the solubility of the element in the liquid metal and the kinetics stage that controls the rate of the dissolution reaction.

The net mass flow rate J, at which a certain element enters the liquid metal, can be described as follows:

\[ J = k (C_o - C) \]  

where:

- \( J \) – the mass flow rate describing the decrease in the concentration of an element, caused by dissolution;
- \( C_o \) – the solubility of the element in the liquid metal;
- \( C \) – the actual concentration of the element in the mass of the liquid;
- \( k \) – a constant that characterizes the mass transfer in the solution (in liquid metal).

Transfer of impurities and alloying elements This process is manifested as a net transfer of alloying elements or impurities to, from or through liquid metal.
Although the compounds may form or dissolve as a result of this transfer, the liquid metal atoms do not take part in the formation of the stable products by reacting with the constituent elements of the structural materials of the equipment. From the thermodynamic point of view, the motor force that causes the transfer of an element between the structural material and the liquid metals is usually expressed through the distribution (partition) coefficient. This distribution coefficient is defined as the ratio between the equilibrium concentration of an element (such as oxygen, nitrogen, carbon or hydrogen) in the solid metal or alloy and the concentration of the same element in the liquid metal. These coefficients can be calculated from the known or estimated free formation energies or from the activities based on the equilibrium between the solid phase and the liquid phase species.

**Alloying**

Reactions between liquid metal atoms and those composing structural material can lead to the formation of a stable solid product without the involvement of the impurities or of the alloying elements.

\[ xM + yL = MxLy \]  

This is not a common form of corrosion in liquid metals, especially in alkali metal melts, but it can have dramatic consequences if it is not well understood or anticipated.

Alloying reactions may, however, be used to inhibit corrosion by adding to the liquid metal an element (corrosion inhibitor) which, by reaction, will form a corrosion-resistant layer on the surface of the steel.

One example is the addition of aluminum to the lithium melt that comes in contact with a metal. Thus, a more resistant dissolving layer (aluminised) will form on the steel surface and thus corrosion will be reduced.

**Reduction of some steel constituents**

The attack of metallic materials exposed to liquid metals can occur due to the reduction of the elements by the melt lead. In the case of very high aggressiveness, such as when most oxides are exposed to liquid lead, the effective result of this exposure is the loss of structural integrity by reducing and removing non-metallic elements from the solid. The tendency for such a reaction to be possible under these conditions can be quantified by taking into account the free energy of solid oxide formation as compared to the oxygen/oxide stability in the liquid metal. Similar considerations apply when assessing possible reactions between other non-metallic compounds (nitrides, carbides and others) and liquid metals.

**Oxygen control**

When the concentration of oxygen in the liquid metal phase is very low, the degradation of the material occurs mainly by the dissolution of the steel constituents. This degradation can be appreciably reduced when a layer of oxides with protective properties is formed on the surface of the steels. In order to facilitate the formation of such a layer, the concentration of dissolved oxygen in the liquid metal must be rigorously controlled. [41] ÷ [58].
Fig. 3 shows the Ellingham diagram which is a useful tool for estimating the optimum concentration of oxygen in the liquid lead so as to avoid undesirable phenomena at the contact between the structural materials and the liquid lead. This diagram shows the dependence of the thermodynamic stability of the oxides of the constituent elements of the steel/alloy, temperature and the concentration of the dissolved oxygen in the liquid lead.

Oxygen is constantly consumed to form oxides on the steel surface, so the concentration of oxygen in the liquid metal must be controlled by appropriate sensors and accompanied by the use of a method of adding oxygen to the liquid metal.

Decreasing the corrosion of steels by the addition of oxygen is applicable only if at least one of the steel components is less noble than the constituents of the liquid metal and the concentration of the less noble steel elements must be large enough to form a layer of continuous and compact oxides on the steel surface.

2. Experiments

There have been tested for corrosion in liquid lead at 450°C for 48 hours, 316L stainless steel and T91 ferrito/martensitic steel. The post - testing examination was realized by optical microscopy and microhardness determinations. The short test time did not require oxygen control. These types of experiments are of particular interest because it is the first time they are done in the RATEN ICN.
3. Results and discussions

The samples were extracted from the liquid lead and exposed in the air. After cooling, the lead solidified on the sample surface and was not removed, [59].

3.1 Visual examination

Fig. 4 shows the surface aspect of the samples that have been maintained in liquid lead at 450 Celsius degrees for 48 hours.

![Fig. 4](image1.jpg)

Fig. 4. Stainless steel 316L – samples tested in liquid lead

3.2 Optical microscopy

The sample surface morphology of 316L and T91 is shown in Fig.5 a) and Fig.5 b) respectively. It is observed that a more consistent layer of lead has been deposited on the surface of the T91 material, which can be explained by the different wetting properties of the surface of the two materials.

![Fig. 5](image2.jpg)

Fig. 5. Morphology of stainless steel 316L (a) and T91 (b) tested in liquid lead.

The thickness of the residual lead layer
For stainless steel 316L, the residual lead layer is irregular with a thickness from 0 to about 24μm, Fig. 6 a). For T91, the residual lead layer is irregular and has a thickness of 0 to about 580μm, Fig. 6 b).

The structure of stainless steel 316L
To highlight the structure, the samples were electrolytically attacked with a 10% oxalic acid solution, 6V, 45-65 seconds. On 316L as-received sample, the presence of equiaxed grain austenite and carbide precipitates was shown, Fig. 7 a). The structure of 316L samples tested in the lead consists of austenite and carbides oriented in the direction of deformation, deformation lines caused by the application of a stress on samples exposed to liquid lead, Fig. 7 b).

3.3 Determinations of microhardness
For the as-received sample, the average Vickers microhardness MHV0.1 is 188 kgf/mm², Fig. 8 a).
For the sample tested in liquid lead, the Vickers microhardness has the value 291 kgf/mm², Fig. 8b). An increase in microhardness is observed for the sample tested in lead, which can be explained both by the action of the temperature and the stress applied to the sample.

Research directions in the field of corrosion of LFR structural materials

- The determination of possible corrosion rates according to:
  - temperature;
  - the flow rate of the liquid metal;
  - the concentration of dissolved oxygen in the liquid lead;
  - other parameters for both ferito/martensitic and austenitic steels.

- The improvement and/or development of techniques/methods to reduce the contamination of the coolant (liquid lead) such as:
  - performant sensors for measuring oxygen concentration;
  - oxygen control systems;
  - specialized filters for the purification of liquid metals.

- The design of new materials with high corrosion resistance at high temperatures to achieve increased thermal and electrical efficiency and other applications (hydrogen production).

- Investigating the degradation of mechanical properties.

- Testing of superficial coatings.

- The determination of degradation at corrosion of the resistance of the structural materials caused by irradiation.

4. Conclusions

- The Generation IV nuclear reactors have some advantages that make them competitive on the energy market in the coming period.

- One of the types of Generation IV reactors that have considerable chances to be realized in relatively short time is the LFR reactor being preceded by the ALFRED demonstration reactor.

- The most challenging aspect of the lead-based technology is the corrosive nature of this liquid metal that requires careful oxygen control and the use of structural materials with high corrosion resistance. The realization of this type of
reactor is overwhelmingly dependent on the solution of the problems with the building materials.

- The main materials that can be used on a LFR equipment can be classified as follows:
  - austenitic stainless steels that are resistant to high operating temperatures specific to LFR;
  - ferito/martensitic steels;
  - Performing ferito/martensitic steels treated thermo-mechanically to determine their sensitivity to fragility;
  - ODS alloys can be an alternative to LFR structural materials, but in the near future their development is not very promising. In addition, these materials are a very expensive solution for some LFR equipments. The development of these materials would be beneficial for the most important components of the primary circuit of the LFR reactors;
  - ceramic materials and refractory alloys.

- To date, the most promising materials are 316L austenitic steel, ferito/martensitic T91 steel and 15-15 Ti austenitic steel.

- Corrosion-specific processes of structural materials that come in contact with liquid lead are as follows:
  - simple dissolution;
  - alloying between liquid and solid metal;
  - intergranular attack;
  - reaction with impurities;
  - mass transfer caused by the temperature gradient;
  - mass transfer determined by the concentration gradient or the coexistence of two different metals in the liquid metal.

- Corrosion in liquid metals can be influenced by many factors, among which the most important are:
  - the ratio between the surface area of the structural material and the volume of the liquid metal;
  - the purity of liquid metal;
  - the flow rate or Reynolds criterion;
  - the state of the surface of the structural material of the process equipment;
  - the number of structural materials in contact with the same liquid metal;
  - the properties of structural material such as: the presence of precipitates at the grain boundary, the presence of a secondary phase, the degree of tension of the material and the size of the grain.

- Corrosion was tested in liquid lead at a temperature of 450°C for 48 hours, 316L austenitic steel and T91 ferito/martensitic steel.

- There was no need for oxygen control in the liquid lead as the exposure time was short and the ratio between the volume of liquid lead and the area of exposed samples had a high value.
After testing, the samples were visually inspected, analyzed by optical microscopy and their microdurality determined.

The optical microscopy showed the following: the morphology, thickness of deposition layer and the microstructure of the tested materials.

The layer thickness of lead had values ranging from $0 \div 24\mu m$ for steel 316L and $0 \div 580\mu m$ for T91.

The average Vickers microhardness MHV0.1 had a value of 188kgf/mm² for 316L for as-received samples and 291kgf/mm² for 316L samples tested in liquid lead.

References


