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# Determination of the protective atmosphere during the Pb–Li alloy remelting

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ABSTRACT

Nuclear fusion technology has been planned as a future massive source of energy. One of the most critical parts of its design is regenerating blanket modules. Among the different materials currently considered for this purpose, we have studied the Pb–Li eutectic alloy. For the production of the eutectic alloy, it is vital to ensure efficient mixing of raw materials, which is hampered by large difference in density of the two components and the high reactivity of Li versus $O_2$. This work addressed this issue by presenting a series of tests were made with eutectic ingots in order to determine the composition of protective atmospheres and crucible material. Alloys manufactured were characterized by microscopy and ICP-MS. The results demonstrate that the best crucible material when making mergers is the SiC, due to the low reactivity presented with Pb–Li. Regarding protective atmosphere, Ar BIP (Built-In Purifier) showed the best protection and can be used in a wide range of temperatures and the eutectic salts improve this protection.



## 1. Introduction

The nuclear fusion technology has been studied since the 1980s and is planned as a future source of energy. Research projects have enabled the development of various experimental facilities [1], which have been the basis for designing, building and operating a thermonuclear experimental reactor (ITER “The International Thermonuclear Experimental Reactor” [2–4]).

Focusing on the ITER project, one of the most critical parts of their design is regenerating blanket “Test Blanket Modules” [5–8], which plays a key role in the future operation of a commercial reactor. The authors of the project propose different TBM concepts that can be grouped into two types according to the physical state in which the breeder material is in the TBM: solid TBM and liquid TBM [9–12].

In the case of a liquid TBM coolant, numerous materials were initially considered: pure Li liquid, the eutectic alloy Pb–Li, $Li_2O$, FLiBe, $Li_4SiO_4$, LiF, $Li_2C_2$, LiCl, $LiAlO_2$, $Li_2SiO_3$, LiAl, $Li_2CO_3$, $LiNO_3$, $Li_3N$, $Li_2TiO_3$ and $Li_2ZrO_3$ [13,14]. After a preliminary selection, depending on design requirements, Li (l), FLiBe and mainly Pb–Li at 15.7 at.% eutectic alloy were considered as candidates. The latter is the material chosen for the TBM in most of the proposals submitted by members of the ITER project [2].

The properties of Pb–Li eutectic alloy define the conditions of its application and breeder blanket design and vice versa, the operating conditions affect the properties of eutectic alloy. Therefore, it is of great interest to establish a database for key specifications and properties according to the QA requirements of nuclear material and considering nuclear system licensing requirements. Some of these properties, such as accurate Li title and structural micro-aggregations, depend on the production process, whose operating parameters must be properly studied and evaluated in order to provide a production route that meets QA standards [15].

In this paper, furnace atmosphere and temperature are considered. The first variable is related to the high reactivity of Li versus $O_2$ leading to the formation of intermetallic species. Temperature is one of the parameters that control the efficiency of mixing hampered by the high density difference of the two components. The crucible material was also studied in order to consider the possible reactivity between this material and the alloy components.

## 2. Materials and methods

Different experiments were performed taken into account the following variables: crucible material, temperature and protective atmosphere.

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**Notations**

| | |
|---|---|
| BIP | Built-In Purifier. |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| ITER | International thermonuclear experimental reactor |
| MHD | Magnetohydrodynamic |
| OM | Optical microscopy |
| QA | Quality assessment |
| SEM | Scanning electronic microscopy |
| SEM-EDX | Energy dispersive X-ray spectroscopy |
| TBM | Test blanket modules |
| XDR | X-ray diffraction |

**Table 1**
Purity and composition of the gas protective used in ppm.

| | Purity % | Ppm $O_2$ | Ppm $H_2O$ | Ppm THC | Ppm CO + $CO_2$ | Ppm $N_2$ |
|---|---|---|---|---|---|---|
| $N_2$ | 99.9992 | 3 | 2 | 0.5 | – | – |
| Ar | 99.9992 | 1.5 | 2 | 0.1 | – | 4 |
| Ar BIP | 99.9997 | 0.01 | 0.02 | 0.1 | 0.1 | 1 |

Several gases (Table 1) and eutectic salts were tested as protective atmosphere. The first test was performed using technical $N_2$, which can only be used at temperatures below 600 °C. In order to increase the melting temperature, Ar (commercial quality and BIP) was used, which can be used up to 800 °C. Finally, the mixture of eutectic salts of KCl/LiCl was tested in air and in Ar BIP.

Several crucible materials were also tested to determine its influence in the process. The next table (Table 2) shows the test performed. All test were performed on previous eutectic alloys, these alloys were produced in the Institute of Physics of the University of Latvia (IPUL), carried out through technology MHD, whose composition varies between 16.9 and 17.31 ± 0.2 at.% Li according to the supplier.

Microstructure variations studies were performed by optical microscopy (OM), Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (SEM-EDX) analysis with detection of light atoms. The OM used was Olympus C304-ADU and the SEM used was JEOL 6400 with Oxford Link Analyzer.

To identify and determine the composition of the crystalline phase present in the alloys, the technique of X-ray diffraction (XRD) was used. The instrument used was a Philips X'Pert, with X-ray source Kα1 of Cu (α) radiation (λ = 1.54.56 Å). The voltage is 45 kV, the intensity is 40 mA and it uses a curve of monochromator Cu.

**Table 2**
Process conditions for obtaining optimal protective atmospheres at different temperatures.

| Group | Test | Temperature (°C) | Time (min) | Gas protector | Crucible |
|---|---|---|---|---|---|
| I | PbLi 0 | 450 | 15 | $N_2$ | C |
| | PbLi 1 | 550 | | | C |
| | PbLi 2 | 650 | | | SiC |
| II | PbLi 4 | 600 | 15 | Ar | SiC |
| | PbLi 3 | 650 | 30 | | $SiO_2$ |
| III | PbLi 5 | 700–800 | 15 | Ar (BIP) | SiC |
| IV | PbLi 6 | 700 | 5 | Ar (BIP) + eutectic salts | SiC |
| | PbLi 7 | 450 | 15 | | |
| | PbLi 8 | 400 | 15 | | |
| | PbLi 10 | 350 | 8 | | |
| V | PbLi 9 | 400 | 3 | Air + eutectic salts | SiC |

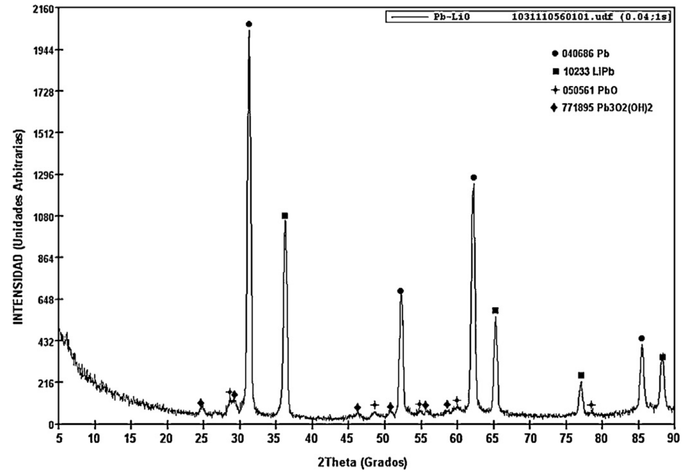


**Fig. 1.** XRD diagram of ingots obtained at 550 °C with $N_2$ such as gas protective.

The lithium content of the alloys was determined by inductively coupled plasma mass spectrometry (ICP-MS) after microwave acid digestion. Analyses were performed in a XSeriesII (Thermo Scientific) mass spectrometer.

## 3. Results and discussion

The test conducted reveals that the best crucible material is the SiC, due to its low reactivity with the alloy PbLi eutectic and their properties [16,17]. The graphite crucibles reacted with the lithium, and the $SiO_2$ crucibles are broken, so the purity of the samples cannot be guaranteed.

The most important variables are protective atmosphere and temperature as discussed here. In the test carried out with technical $N_2$ at low temperatures (450–550 °C), a complete melting of the alloy is not achieved, and at higher temperatures (650 °C), the surface is blackened due to high lead oxide formation. This can be seen in the XRD diagram shown below (Figs. 1–2).

The micrography, obtained by SEM, shows that at low temperatures the eutectic structure – with laminar microstructure α-Pb + β-LiPb – is maintained (Figs. 3–5) and, at high temperatures, oxidation increases and lithium is lost and hypoeutectic structures with primary dendrites of α-Pb in a laminar eutectic microstructure α-Pb + β-LiPb matrix are formed (Fig. 6).

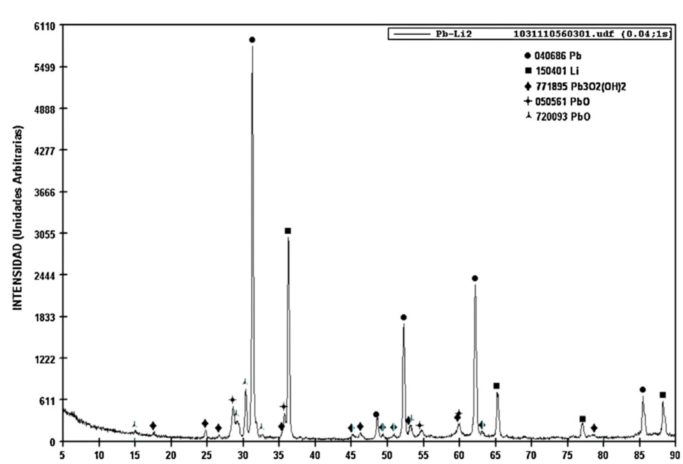


**Fig. 2.** XRD diagram of ingots obtained at 650 °C with $N_2$ such as gas protective.