Electrochemical measurement and characterization of corrosion products in lead-bismuth eutectic

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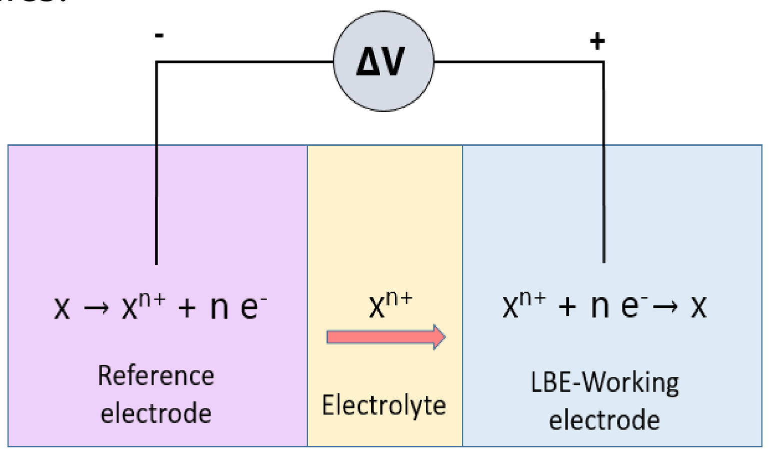
Methods

Dissolved metallic elements in liquid metals can be selectively detected by a potentiometric sensor based on metallic cation conducting electrolyte, which can be either liquid state, *i.e.* molten salts, or solid state, i.e. ion-conducting ceramics.



Nernst Law

$$\Delta V = -\frac{RT}{nF} \cdot \ln(a_{X,LBE})$$

Solid electrolytes conducting transition metal cations are for instance NASICON-like conductors and doped β''-alumina.

Beta-alumina is a family of fast sodium conductors, Na-β-Al_2O_3 ($NaAl_{11}O_{17}$) and Na-β''-Al_2O_3 ($NaAl_5O_8$), that can conduct various monovalent (in β and β'') or polyvalent (in β'') cations if Na^+ is replaced by an ion-exchange process such as:

1) Vapor phase ion exchange
2) Liquid phase ion exchange
3) Liquid phase ion exchange coupled with coulometric titration

Introduction

MYRRHA (Multi-purpose hYbrid Research Reactor for High-tech Applications) is the first prototype in the world of an Accelerator Driven System (ADS) cooled by liquid lead-bismuth eutectic alloy (LBE).

LBE exerts corrosive effects on the structural steels of the reactor by dissolving the main alloying elements: Ni, Fe, Cr and Mn. These impurities, reacting in LBE to form intermetallic or oxide compounds, contaminate the coolant and change its thermohydraulic properties.

Analytical methods need to be developed for the on-line monitoring of metallic impurities in LBE, as well as for the study of their thermochemical and transport properties in liquid metals.

Objectives

The goal of this PhD is to develop electrochemical sensors to characterize the metallic corrosion products (mainly Fe and Ni) monitoring *in-situ* the concentration and determining the main thermochemical properties.

Measurable variables:
- Impurity concentration
- Activity coefficient
- Solubility
- Diffusion coefficient

Results

Ion-exchange process optimization

Several Na-β"-Al_2O_3 tubes were subjected to liquid and vapor phase ion-exchange with $FeCl_2$ and $NiCl_2$ in various conditions.

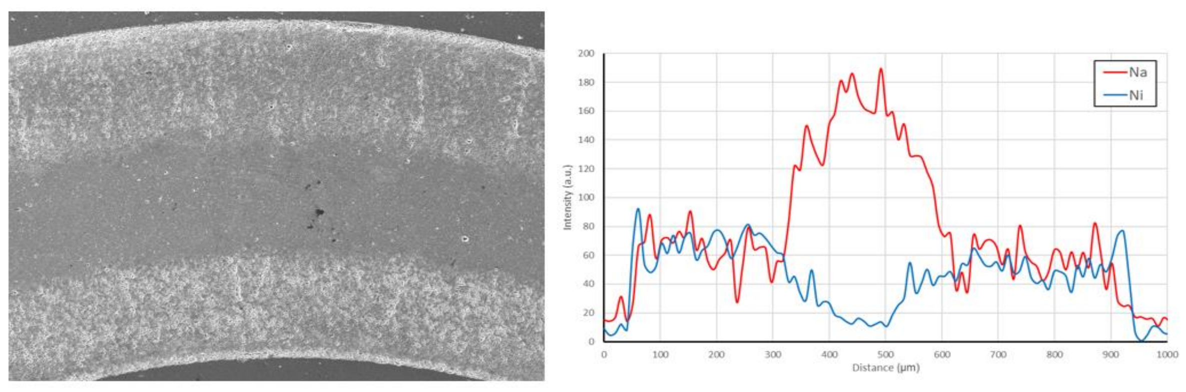
Doped β"-Al_2O_3 characterization

Cross-section of ion-exchanged samples was analyzed with different microscopy techniques to evaluate the ion exchange through the lattice.

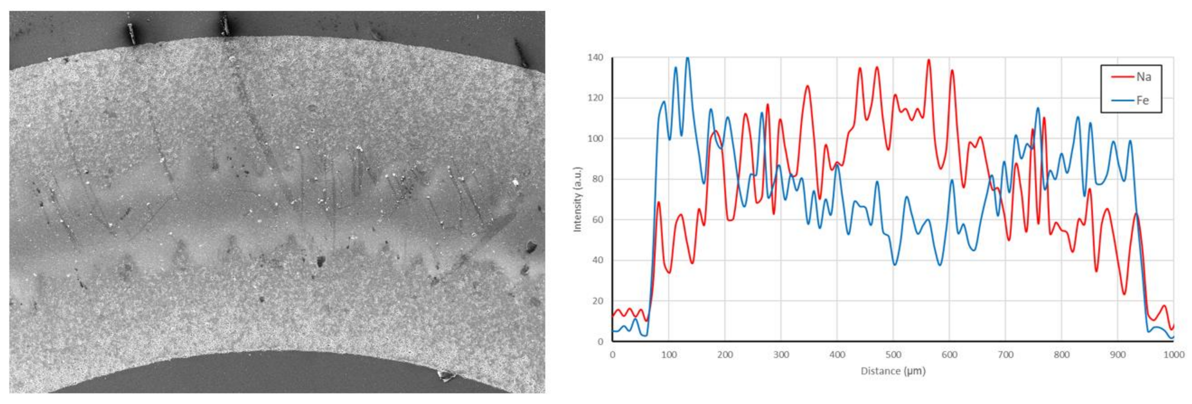
1) Optical microscopy: Color change can be seen throughout the sample cross-section, Ni-β"-Al_2O_3 appeared blue and Fe-β"-Al_2O_3 brown, whereas pristine Na-β"-Al_2O_3 was white.

Liquid exchanged Ni-β''-Al_2O_3 (left), vapor exchanged Ni-β''-Al_2O_3 (middle) and liquid exchanged Fe-β''-Al_2O_3 (right)

2) SEM-EDS: Cross-section of ion-exchanged samples was analyzed with electron microscopy to evaluate the doping yield and the effects on microstructure. The distribution of doping element through the cross-section was obtained with SEM-EDS analysis.



SEM-EDS characterization of liquid exchanged Ni-β''-Al_2O_3 cross-section



SEM-EDS characterization of liquid exchanged Fe-β''-Al_2O_3 cross-section

- Ion-exchange yield was lower in the inner region of the β"-Al_2O_3 than in the external one. The penetration of doping cations is influenced by the reaction environment, the activity of dopant in the salt, the reaction temperature and the exposure time.
- Fe was doped successfully through the entire cross section by liquid phase ion exchange in molten $FeCl_2$, even if a lower yield was obtained in the inner region. The highly doped outer region, however, showed a porous microstructure.
- Nickel doping was conducted in molten NaCl-$NiCl_2$ mixture due to the high melting temperature of pure $NiCl_2$. The depth of Ni doping by the liquid phase ion exchange was limited to 200 µm even at higher temperatures and longer exposure times. Vapor phase ion-exchange with pure $NiCl_2$ showed better yield compared to the liquid phase doping with NaCl-$NiCl_2$ mixture.

Discussion

Generally divalent and trivalent cations show a lower mobility in β"-Al_2O_3 lattice compared to monovalent cations. Thus the dopant depletion in the inner region of sample cross-section could be explained by the limited diffusion of divalent Ni^{2+} and Fe^{2+} cations through the ceramic bulk. The porous microstructure in the highly doped regions is likely attributed to a consequence of lattice parameter change occurring when Na^+ (r_{ion}=116 pm) is replaced by smaller Ni^{2+} (r_{ion} = 83 pm) or Fe^{2+} (r_{ion} = 75 pm), leading to a compression of crystal structure. Although liquid phase ion exchange, performed in molten $FeCl_2$, can be a suitable process to prepare Fe-β"-Al_2O_3, it turned out not to be applicable for Ni-β"-Al_2O_3. when performed in liquid mixture NaCl-$NiCl_2$.

Conclusion

Ni-β''-Al_2O_3 and Fe-β''-Al_2O_3 are expected to be promising solid electrolytes for metallic impurity sensor in liquid metals. The first part of this PhD is aimed at optimizing the nickel and iron ion-exchange process of Na-β''-Al_2O_3 tubes. Liquid phase ion-exchange in molten $FeCl_2$ provided a consistent doping yield through the whole tube cross-section, even if it was lower in the inner region, whereas it only involved the external surface when performed in the liquid NaCl-$NiCl_2$ mixture. Vapor phase ion-exchange with $NiCl_2$ provided more homogeneous doping up to the inner region of the ceramic sample.

Future work

- Nickel vapor ion-exchange improvement: test at different pressures and temperatures in sealed environment.
- Reference electrode material validation: metallic powder or metal-saturated liquid bismuth.
- Sensor test in LBE: demonstration of technique feasibility