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Corrosion in liquid metals: from database acquisition to life time prediction

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1. INTRODUCTION

In nuclear power plant, materials can be corroded by liquid metals that are either flowing as coolant in first and secondary circuit (lead alloys: Pb-Bi) or stagnant as fission product in cladding (tellurium). Steel corrosion process depends: (i) on the concentration of dissolved corrosive element as O or C that can lead to oxidation or carburization, similarly to corrosion processes in gas phase; (ii) on the potential existence of intermetallic containing elements originating from both liquid metal and steel ($FeTe_2$, Cr_3Te_4); (iii) on capability of steel dissolution in the liquid metal. For all these corrosion processes, thermodynamic databases have to be developed in order to model the corrosion mechanisms. The obtained corrosion model is supposed to be used for life time prediction. This paper deals with both thermodynamic data acquisition (Ni solubility limit in liquid lead bismuth alloy) with thermodynamic database development (Calphad method) and corrosion experiments with mechanism modelling. Liquid metal environment considered are liquid Te and Pb-Bi alloy. Corroded steels are austenitic steels.

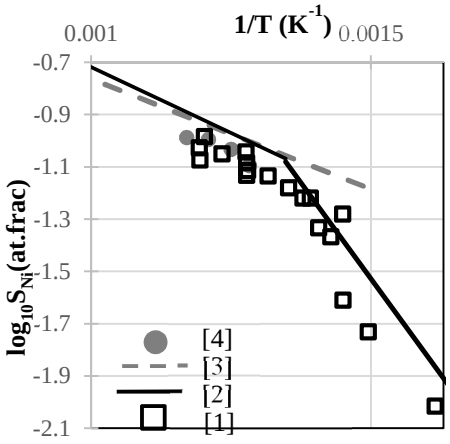


Fig 1: measured and calculated solubility limit (Calphad method) of Ni in Pb-Bi alloy [1-4]

2. EXPERIMENTAL

Corrosion experiments are carried out in stagnant liquid metal conditions in crucible in glove box at 500°C and 551°C for respectively Pb-Bi alloy and pure Te. Ar or Ar-H_2 gas are sweeping over the liquid metal to avoid steel oxidation. Samples dimensions are 30x10x(0.5 or 1) mm. Two experimental techniques have been implemented for the determination of the nickel solubility limit in Pb-Bi at low temperatures. The first one is performed from 400°C to 500°C using Laser Induce Breakdown Spectroscopy (LIBS). The LIBS technique permits to obtain in situ measurements directly performed on liquid Pb-Bi. It allows to monitor on line the concentration of the dissolved impurities in the liquid coolant. However, this technique is still under development and optimization for liquid media. The second technique is ICP-AES. It is commonly used to analyse alloys composition. It permits a very reliable analyse of a Pb-Bi sample. However, ICP-AES analysis is ex-situ. The investigated temperatures for nickel solubility limit measurement via ICP-AES ranges from 350°C to 535°C. For technical reasons, the experiments could not be performed above 535°C.

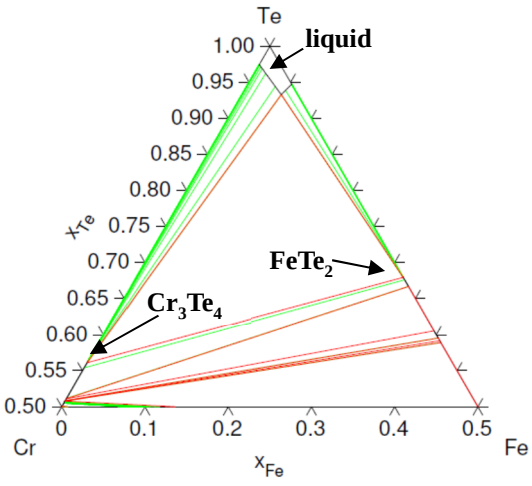


Fig 2: Te rich domain of the ternary Te-Cr-Fe phase diagram calculated at 550°C (Calphad method)

3. RESULTS AND DISCUSSION

3.1. Thermodynamic data acquisition

Ni solubility limit has been measured in Pb-Bi eutectic and then compared to literature data (Fig 1.) [1,2].
The solubility limit law, obtained for the highest temperatures, is in agreement with the literature data [3,4] for the same temperature range.
In this study, a change of slope in the solubility limit law (Fig 1) is obtained at lowest temperatures. In order to better predict the metals (Cr-Fe-Ni) solubilities at equilibrium, thermodynamic modelling has been performed using the Calphad method [2]. According to this modelling, the Ni solubility exhibit a change of slope due to the precipitation of BiNi intermetallic at low temperature (instead of FCC-Ni at higher temperature).
For corrosion in pure Te, Cr-Te and Fe-Te binaries have been modelled [5]. The ternary phase diagram Cr-Fe-Te is calculated by extrapolation of these binaries.
To predict the phases at equilibrium, the isothermal Cr-Fe-Te cross section is calculated in the Te rich domain (Fig 2). The diagram is plotted at 550°C that is the temperature of interest for corrosion experiments. Results show the presence of a three phase domain where liquid Te equilibrates with two Cr-Te and Fe-Te intermetallics: Te_{liq} + Cr_3Te_4 + $FeTe_2$.

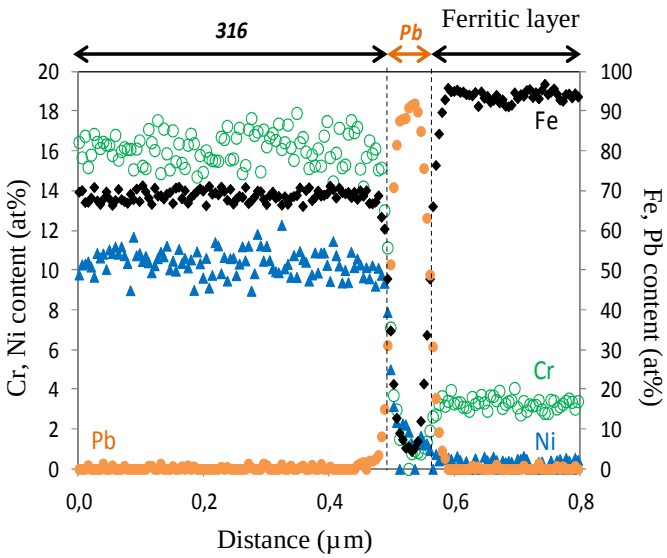


Fig 3: TEM-EDX profile of 316L sample corroded 1470 h in Pb-Bi at 500°C.

3.2. Corrosion tests and modelling

Corrosion of 316L in liquid Pb-Bi with low oxygen concentration leads to pure dissolution of the steel. However the dissolution is not congruent. Preferential dissolution of Cr and Ni leads to phase transformation from austenite to ferrite of 316L in contact with Pb-Bi (Fig 3). For all tested austenitic alloys, corrosion kinetics are linear and Cr dissolution rates have been measured and are presented as a function of Cr activity of steels in Fig 4. It shows that the Cr dissolution rate is proportional to the Cr activity in the steel. In order to determine the corrosion mechanism, the corrosion rate has been modelled considering that it is controlled by diffusion of dissolved Cr across the diffusion boundary layer generated by natural convection of the liquid metal. Fig 4 shows that the calculated corrosion rate is also proportional to the steel Cr activity and approximately twice the experimental one. Then diffusion of Cr in diffusion boundary layer could control the corrosion rate of the various studied austenitic steels.

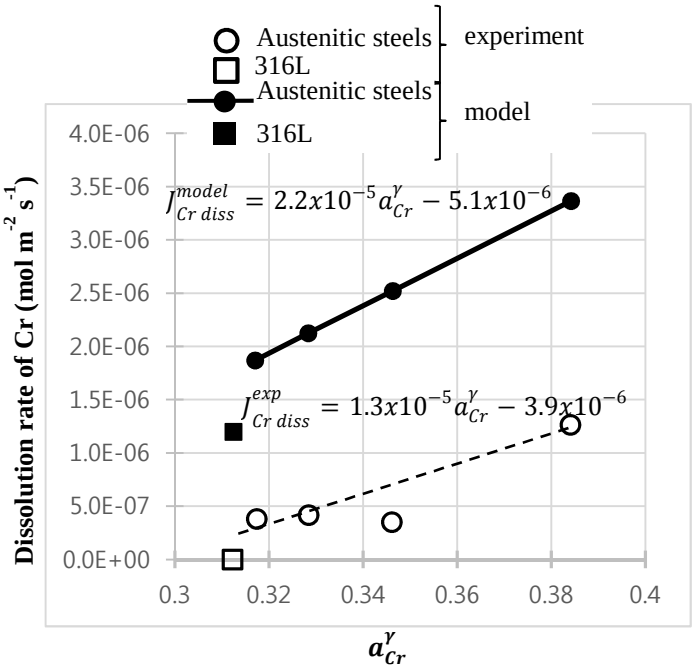
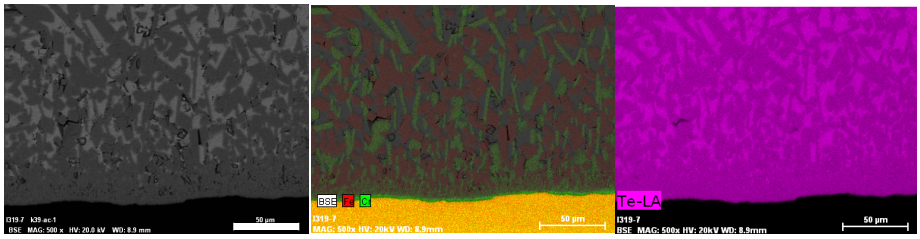


Fig 4: experimental and modelled corrosion rate of austenitic alloys in liquid Pb-Bi.

For corrosion of 316L in pure Te, thermodynamics (Fig 2) forecasts formation of two intermetallic phases as Cr_3Te_4 and $FeTe_2$. Indeed, EDX map of Fig 5 shows that a Te-Cr layer is formed at the 316L/Te interface. This layer is topped by a complex mixed Cr-Fe-Ni-Te intermetallic layer. However all phases have $(Fe,Ni,Cr)Te_2$ stoichiometry. During cooling, solidification of Te led to precipitation of several Cr-Ni-Fe-Te intermetallics as $(Fe,Ni,Cr)Te_2$ phases (Fig 5). The corrosion rate of 316L is mainly due to congruent dissolution of the steel. The adherent intermetallic layer seems porous. Model of this corrosion rate has been done considering that: (i) the corrosion rate is controlled by the reaction rate of iron dissolution; (ii) the corrosion rate is controlled by diffusion of iron in liquid Te. Calphad method used to fit experimental data from literature (Fig 2. Part 3.1) permitted to obtain better estimation of the iron solubility limit used in the two models. In Fig 6, both models are fitted on experimental concentration of dissolved Fe coming from corrosion of 316L. From these two fits, the diffusion coefficient of Fe in Te (diffusion model) and the apparent reaction rate constant (interface reaction model) are obtained and equal to, respectively: 10^{-5} cm^2 s^{-1} and $7x10^{-4}$ s^{-1}. The obtained diffusion coefficient agrees with the usual values of diffusion coefficients in liquid. Moreover this model presents a better fit on experimental results. On this basis, it is concluded that Fe diffusion in the liquid Te controls the 316L corrosion rate.



(a) QBSD image (b) Fe and Cr map (c) Te map

Fig 5: SEM-QBSD image of cross section of 316L after immersion in the melt for 30 min.

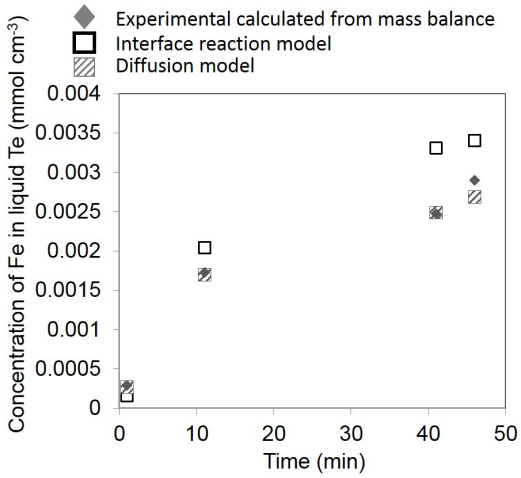


Fig 6: calculated concentration of experimentally dissolved Fe from mass balance for various corrosion time; corresponding models considering a control by interface reaction rate or by Fe diffusion in liquid Te.

4. CONCLUSION

Determination of thermodynamic and kinetic database are necessary in complex media as liquid metals. They are used in mathematics model, firstly to discriminate the possible corrosion mechanisms and secondly to evaluate the life time of components. In this study, corrosion of 316L and other austenitic steels (for corrosion in Pb-Bi) in stagnant pure Te and Pb-Bi alloy seem to be controlled by the diffusion of dissolved species in the liquid.

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