Titolo
CARATTERIZZAZIONE E MODELLING DEI PROCESSI DI OSSIDAZIONE IN METALLO LIQUIDO PESANTE

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Sommario
I meccanismi che governano la corrosione dell’acciaio in metallo liquido non sono ancora del tutto compresi, nonostante i numerosi studi sperimentali e i crescenti studi computazionali riportati in letteratura sull’argomento. L’attività condotta da POLIMI si è concentrata sulla valutazione dello stato dell’arte sia nell'ambito di attività sperimentali che computazionali relative alla caratterizzazione dell’interfaccia piombo-acciaio, al fine di proseguirne l’indagine attraverso un approccio teorico che quindi affianchi le attività sperimentali svolte da ENEA.

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Caratterizzazione e modelling dei processi di ossidazione in metallo liquido pesante

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Introduction

A computational approach combined with the experimental activities could contribute to the understanding of the mechanism of growth of oxide layers on the surface of steels in oxygen-containing lead melts, that is still unknown. With this purpose, POLIMI performed a literature analysis in order to highlight what are the experimental evidences already reached and identify the aspects towards which the computational approach could be addressed.

Experimental studies

In literature several experimental studies are present dedicated to understand the different aspects involved in liquid metal corrosion phenomena, such as corrosion mechanisms, corrosion product solubility, diffusion and transport, environmental effects and oxygen control technology for steel corrosion mitigation. [Zhang 2008]

Loss of steels in liquid Bi, Pb or LBE occurs primarily through dissolution of steel components into the liquid when there is no erosion due to the flow. The main driving force for liquid metal corrosion is the chemical potential for dissolution of all solid surfaces in contact with the liquids. The compositional and microstructural changes due to selective dissolution and intergranular corrosion can lead to material failures. The dissolution rate depends on the liquid media, the ratio of the surface area of the solid metal to the volume of the liquid metal in a static solution, the flow rate in a dynamic solution, the surface conditions of the steel, the content of interstitial impurities such as oxygen and nitrogen in the liquid metal/alloy and the compositions of the solid materials. When liquid metals flow over solid material surfaces, corrosion is accelerated by the velocity of liquid metals. This is termed as flow accelerated corrosion (FAC). There are a number of mechanisms for interactions between the flow and dissolution. The combination of different mechanisms results in four main types of flow accelerated corrosion: mass transport-controlled corrosion, phase transport-controlled corrosion, erosion–corrosion and cavitation–corrosion. [Baldud 2001]

Liquid metal corrosion process may involve the following four processes:
1. Dissolution of the solid materials into the liquid metal.
2. Thermal and concentration gradient assisted mass transfer in liquid and solid.
3. Redistribution of the interstitial impurities between the solid and liquid metals.
4. Diffusion penetration of liquid metals into solid metals with formation of solid solutions or new phases.

The operating conditions determine which process dominates, and the factors affecting one of the above processes should affect the corrosion rate.
For static corrosion tests, the transport process is mostly diffusion that depends on the corrosion product concentration gradient and the corrosion product diffusion coefficient in liquid metal. When the dissolution rate is less than the diffusion rate, the diffusion is fast enough to take all the dissolved species and the corrosion rate is determined by the dissolution rate. Otherwise, the concentration at the interface is
always at saturation and the corrosion rate is determined by the diffusion rate. In liquid metal systems there is good evidence that both cases described above occur depending on both the solution and solute. The situation is quite different in a flowing system. Corrosion products can be transported by both diffusion and convection from corrosion locations to other places where the corrosion products may deposit. Among external factors influencing corrosion, the flow velocity is of the most importance. [Zhang 2007, Heitz 1991, Weber 1992] It is evident from experimental research that temperature plays an important role: increasing temperature results in higher dissolution rates, higher solubilities, higher diffusion coefficients, leading to higher corrosion rates. [Gomez 2001] The general approaches to reduce the corrosion of structure materials in liquid metal system are mainly improving anti-corrosion properties of the structure materials and reducing corrosive effect of the liquid metal, such as by adding inhibitors or controlling oxygen. Experimental results on the corrosion of different steels in static and flowing liquid metal [Glasbrenner 2001], with or without inhibitors, are still scattered, however some general considerations can be inferred:

- For very low oxygen levels (<10⁴ ppm), both austenitic and martensitic steels in LBE are subject to dissolution even at temperatures as low as 673 K. The dissolution rate of the austenitic steel is less than that of the martensitic steel.
- In the temperature range of 573–743 K, protective oxide films can form on austenitic and martensitic steel surfaces at oxygen levels above 10⁴ ppm. The thin oxide films can protect the steel elements against rapid dissolution of steel components into LBE. The protective layer for martensitic steels is much thicker than that for austenitic steels.
- Generally, the oxide films on martensitic steel have a double-layer structure: an outer porous layer of magnetite and an inner compact layer of Fe–Cr spinel. The films grow at both interfaces: the LBE/oxide interface and the oxide/steel interface. The oxide films on austenitic steel surfaces are mostly composed of Fe–Cr spinel at lower temperatures.
- At 823 K, dissolution is observed for AISI 316L steel in static LBE with saturated oxygen, while double-layer oxide films were found in flowing LBE.
- For temperatures above 823 K, heavy dissolution corrosion of austenitic steels occurs and these steels cannot be used without special treatments. If the steel surface is alloyed with Al to form FeAl alloy or treated using the GESA method, a protective oxide layer can form even at 873 K. Although the durability of such protective films is good for the test durations of a few thousand hours, it is not clear that they can be ‘self-healing’ if failures occur. [Zhang 2009]
- For martensitic steels, very thick oxide films form on the surfaces if the temperature is above 823 K. This indicates that long-term applications of these steels in their original states may be problematic since thick oxides are not very protective and will become unstable.
- Between 750 K and 823 K, a transition temperature or temperature range exists in which the corrosion mechanism changes from oxidation to dissolution. It is possible to form the protective oxide layer on steel surfaces.
The corrosion behaviors depend on the steel compositions, the steel surface treatment, the oxygen concentration in LBE, etc.

- For long-term operations, the scale removal due to the flowing LBE has to be considered. The presence of liquid metal can either enhance or reduce the oxidation rate constant, which may lead to different oxide layer structure and thickness from the oxide layer in gaseous environments.

Based on the experimental results, the possible oxide layer structures of steel in LBE are shown in Figure 1.[Barbier 2001, Muller 2002, Muller 2004, Muller 2000]

For systems with oxygen control, the oxygen is transported by both diffusion and convection to steel surfaces. At the beginning, oxidation and dissolution may occur simultaneously. If the oxidation process is favored and dominates, protective oxide films form on the steel surface. Once the oxide films form, the direct dissolution is reduced significantly because the film separates the steel surface from liquid metal.

For such cases, iron diffuses through the oxide layer, as shown in Figure 2, and formation or dissociation of magnetite occurs at the oxide/liquid metal interface at the same time. With increasing time, the oxide layer becomes thicker and the diffusion rate of iron through the oxide layer becomes smaller because of the increasing

![Figure 1. Possible oxide structures of stainless steels in liquid lead alloys with oxygen control: (a) single layer, (b) single layer, selective oxidation, (c) duplex layer and (d) no oxide layer.[from Zhang 2008]](image1)

![Figure 2. Oxide layer forms at the steel/liquid metal interface.[from Zhang 2008]](image2)
thickness. As reported in other literature works, in a process at 650°C with chromium steel in stagnant lead saturated with oxygen, the initial stages of interaction are characterized by the formation of islands of double oxides (Me₃O₄ where Me: Fe, Cr, Pb) on the steel surface. [Eliseeva 2005] In the course of time, as a result of the lateral growth of the islands, the surface becomes completely covered with a double oxide layer. The outer part of the layer formed by a (Fe₁₋ₓPbₓ)O · Fe₂O₃ complex compound grows from the initial "solid-metal–melt" interface toward the liquid-metal medium. The inner part of the layer formed by the (Fe₁₋ₓPbₓ)O · (Fe₁₋ₓCrₓ)₂O₃ spinel enriched with chromium (see Figure 3) grows toward the matrix. The processes of growth of the outer and inner parts of the double oxide layer are correlated and, in fact, symmetric relative to each other. Lead is present only in the double oxide layer and does not penetrate into the steel matrix.

![Figure 3](image)

**Figure 3.** Schematic diagram of growth of the double oxide layer on the surface of 20Kh13 steel in the lead melt saturated with oxygen at 650°C. [Eliseeva 2005]

Regarding plumboferrites, some experimental works partially built the phase diagram of the system PbO-Fe₂O₃, largely by X-ray diffraction analysis. The results indicate the existence of three intermediate phases: a phase (beta) extending from PbO·5Fe₂O₃ to PbO·6Fe₂O₃, with the same structure of magnetoplumbite; a phase (gamma) extending from PbO·2Fe₂O₃ to PbO·21/2Fe₂O₃, with a not well known structure, and a phase (delta) 2PbO·Fe₂O₃, that has a tetragonal crystal structure. [Mountvaka 1962, Diop 2010, Gerber 1994]

**Preliminary Raman and XRD characterizations**

Preliminary Micro-Raman and XRD characterizations have been carried out by ENEA on grade 91 martensitic steel samples after exposure to oxygen saturated lead at 550 °C. The Raman measuring apparatus allows to perform measurements with micrometer resolution using a Raman microscope excited by a laser Nd: YAG duplicated (wavelength 532 nm). The spectra obtained experimentally in different points of the sample were compared with those available in the literature and databases, and several compounds belonging to the family of lead chromates and lead oxides have been then identified. The XRD data also showed the presence of weak peaks non indexable as steel or iron and iron chromium oxides. The weakness of the signals, broadening of the peaks and the multitude of possible compounds makes difficult the univocal identification of the spectra. Further experimental work is needed and will be carried out with the support of the theoretical investigations carried out by POLIMI.
Microstructural characterizations by transmission electron microscopy will be also carried out with electron microdiffraction experiments for the identification of the phases and in imaging mode to study their spatial distribution in the volume of the oxidized layer in the sub nanometer range.

**Preliminary computational activities**

After having identified the composition and structure of the layer formed at the lead-steel interface, POLIMI investigated the possibility to study the properties of such compounds by computational simulations, starting from what is already present in literature. The main crystal structures of interest are the spinel structure and, due to the high presence of Fe, the inverse spinel-type structure of magnetite (Fe₃O₄). As consequence of oxygen, also hematite (Fe₂O₃) and plumboferrites (nPbO–mFe₂O₃) have to be considered.

Several works in literature deal with the general structure of AB₂O₄ (A²⁺, B³⁺), having a prototype in MgAl₂O₄.[Sickafus 1999] It has a close-packed face-centered cubic structure with cations occupying 1/8 of the tetrahedral sites and 1/2 of octahedral sites. MgAl₂O₄ exhibits good resistance properties and high melting point (1250 °C), and computationally it has been possible to relax the structure and find lattice parameter with a little error, by finding the minimum of energy curve vs lattice parameter using Wien2K code, as well as to investigate the electronic and optical properties.[Hosseini 2008] Their thermodynamical properties were studied both experimentally and computationally with a good agreement.[Barin 1995, Reshak 2014].

Several papers employed computer modelling techniques based on the density functional theory to study magnetite and calculate the geometries and surface free energies of a number of surfaces at different compositions, including the stoichiometric plane, and those with a deficiency or excess of oxygen atoms.[Santos-Carballal 2014] Quantum mechanical calculations were performed with VASP code within the usual Kohn–Sham (KS) implementation of DFT and the results are in good agreement with previous experiments.

A study reported on the spinel-type compound mainly present between magnetite and steel indicate as these compounds present a percentage of Cr and Ni that change the magnetic properties of spinel structure [Robbins 1971]. A model was developed in order to evaluate thermodynamics properties in a different cation order [Kurepin 2005]. The results obtained show that cation distribution and properties depend on Fe²⁺ and Cr³⁺ interaction. Calculations based on Density Functional Theory were used to evaluate thermodynamic properties with a good agreement with experimental data [Andersson 2013]. As previously said, at the lead-steel interface Fe₂O₄ is the external layer so having a role of protection to corrosion. Using first-principle study by means of VASP package code, it is possible to calculate different energy formation of defect and diffusion of atoms in bulk as reported in literature.[Li 2016] This study indicate that the penetration of those atoms in protective films promotes point defects formation and accumulation and, as a net effect, a decreasing anti-corrosion ability of Fe₂O₄. The partial removal of protective oxide layer depends on the interaction between magnetite and liquid metal. By means of VASP code the absorption energy of Pb on Fe₂O₄ surface was evaluated enabling to better
understand what happens at magnetite interface and conclude about what process or absorption is more favorable.[Li 2014]

Another atomistic approach that could led to acquire useful information is molecular dynamics (MD). This method consists in calculating atom positions and velocity of the motion of all atoms involved in a system on the basis of Newton’s second laws as a function of time-step or phase space trajectories of atoms, which can be used to determine the properties of materials. The initial data are taken as the initial coordinates and velocity of all the atoms and the interatomic potentials. From this it is possible to study how the system evolves by knowing potential and interaction between atoms that are the output of simulations. A lot of research works in literature faced irradiation effects by analyzing Frenkel pair formation, PKA energy and cascade starting from collision particles mass, direction, fluence and energy. [Grechanovsky 2013, Voskoboinikov 2013, Buchan 2015] Other works focus on corrosion phenomena. For example, [Maulana 2008] investigate different capacities of penetration of Pb and Bi in surface of a simulated steel with different percentage of Ni and Cr, finding that diffusion dependence on temperature and impurities presence. A quite recent work considers the effect of oxygen injection into lead coolant to reduce the corrosion rate of Fe at different temperature, underlying the importance of oxygen in reducing diffusion coefficient of Fe and so in reducing corrosion. [Arkundato 2013] In this paper authors applied MD simulation method to calculate the diffusion coefficient of corrosion. Even if the application of MD simulation method to study the corrosion of liquid metal is relatively new, it represents a promising research topic.

Conclusions

Considering the state of the art synthetically described above, POLIMI will start new computational studies, taking into consideration the experimental evidences and needs coming from the experimental activities performed within the PAR projects. The future activities will be based on the application of DFT theory for the study of thermodynamic properties of the complex oxides formed as consequence of corrosion. Computational details reported in the selected papers represent the starting point for the computational activities to be developed. Moreover, following the promising results reported in literature about the interesting application of MD to the corrosion topic, attempts will be made to apply the molecular dynamic approach for investigating the penetration and diffusion phenomena that take place in HLM corrosion of steels. The theoretical work will be supported by the optical spectroscopy and microstructural TEM and XRD characterizations performed by ENEA.
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Curtriculum gruppo di lavoro CIRTEN - POLIMI


Marco Giola ha conseguito il Diploma di Perito Industriale, a indirizzo Chimico, nel 1983. Dal 1987 lavora presso il Laboratorio di Radiochimica e Chimica delle Radiazioni in qualità di Collaboratore Tecnico. Ha conseguito una pluriennale esperienza sia in laboratorio chimico tradizionale che in ambito radiochimico operando con soluzioni e matrici radioattive.

Elena Macerata si è laureata al Politecnico di Milano nel 2004 in Ingegneria Nucleare (laurea quinquennale) con indirizzo “Impianti a Fissione e Sistemi a Fusione”. Nel 2008 ha conseguito il titolo di Dottore di Ricerca in Scienza e Tecnologia delle Radiazioni (XX Ciclo), presso il Dipartimento di Energia – Sezione Nucleare del Politecnico di Milano, presentando una tesi dal titolo “Study of calixarene-based picolinamide ligands for An(III)/Ln(III) separation”. Dal 2008 è assegnista di ricerca presso il Laboratorio di Radiochimica e Chimica delle Radiazioni. È autrice o co-autrice di 13 pubblicazioni su rivista internazionale e proceedings di conferenze nazionali ed internazionali.

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Stefano Matteo Cervino sta svolgendo la tesi di Laurea Specialistica in Ingegneria Nucleare presso il Laboratorio di Radiochimica e Chimica delle Radiazioni sullo studio teorico delle proprietà termodinamiche dei composti formatesi all'interfaccia cladding-coolant e alla possibile modelizzazione del fenomeno di corrosione in metallo liquido.

Le attività di ricerca scientifica, prevalentemente sperimentali, del gruppo riguardano:
- Caratterizzazione di matrici contaminate da waste nucleari e/o industriali: separazione e determinazione di analiti e/o radionuclidi;
- Determinazione e speciazione di isotopi in traccia e ultra-traccia mediante ICP-MS e HPLC/ICP-MS; studio e modellizzazione di processi chimico-fisici-tecnologici e di migrazione di contaminanti mediante radio traccianti;
- Valutazione di rischio radiologico nello smantellamento di impianti nucleari e industriali interessati da contaminazione da radionuclidi artificiali e naturali (NORM);
- Studio e realizzazione di dosimetri chimici per le dosi industriali di trattamento-sterilizzazione e per la diagnosi e la terapia medicale;
- Chimica delle Radiazioni: Studio di modificazioni radioindotte, con tecniche chimico, fisiche e nucleari, di materiali impiegati in applicazioni tecnologiche e sanitarie.

L'attività di ricerca di base ed applicata è svolta sia all'interno di collaborazioni scientifiche che in progetti e contratti di ricerca finanziati e/o co-finanziati da istituzioni (EC, MIUR, PRIN), enti ed importanti aziende (ENI, ENEA, SOGIN, FIAT, AITEC). In particolare, il gruppo di ricerca ha acquisito esperienza pluriennale e consolidata nell'ambito dei processi separativi avanzati. Nei processi di tipo idrometallurgico, sviluppati nella strategia di Partitioning & Transmutation (P&T) del combustibile nucleare esaurito, e nei processi di Conditioning di rifiuti nucleari derivante dal riprocessamento pirochimico, collaborando con numerosi Partners italiani ed europei (ENEA, CEA, FZK, FZJ, CIEMAT, UNIREADING, UNICHALMERS, etc.) nei progetti nazionali MIUR e MSE-ENEA-CIRTEN e in quelli europei NEWPART (4° FP), PARTNEW (5° FP), EUROPART (6° FP), ACSEPT e SACSESS (7° FP).