UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN

The Grainger College of Engineering
Department of Nuclear, Plasma, & Radiological Engineering
Suite 100 Talbot Laboratory, MC-234
104 S. Wright St.
Urbana, IL 61801

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Review of Doctoral dissertation by Mr. Michał Komorowicz
„High-temperature corrosion of ceramic construction materials for Dual Fluid Reactor"

The doctoral dissertation submitted for review concerns the corrosion of ceramic materials, especially silicon carbide (SiC), by liquid metal in the Dual Fluid Reactor (DFR) technology. The thesis presents the concept and characteristics of the DFR, which uses a metallic eutectic fuel with chromium and a lead coolant and operates at high temperatures and low pressures. The author investigates the corrosion mechanisms and interactions between SiC and lead, using both theoretical simulations and experimental tests. The thesis shows that the cubic SiC (3C-SiC) has lower resistance to lead-induced corrosion than other polymorphic forms, and that the oxidation of SiC forms a protective silica layer at moderate temperatures and oxygen concentrations. The thesis also describes the design and requirements of a micro demonstrator loop facility, which aims to conduct corrosion tests on different SiC samples under realistic conditions. The reviewed work reliably and systematically analyzes which of the proposed solutions has the best features in theoretical and practical application, which are decisive factors for the success of wide implementation of a given technology in the energy industry.

The PhD thesis is about the corrosion of ceramic materials, especially silicon carbide (SiC), by liquid metal in the Dual Fluid Reactor (DFR). There are several aspects of relevance and importance of this thesis within the context of Polish, EU, and international nuclear energy. First, the DFR is a novel concept of a fast nuclear reactor that uses liquid metal fuel and coolant, which offers advantages such as high efficiency, fuel breeding, waste reduction, and passive safety features. The EU supports the development of innovative nuclear technologies, such as the DFR, through its research and innovation framework programs, such as Horizon 2020 and Euratom. The EU also cooperates with non-EU countries and international organizations on nuclear safety, security, and non-proliferation, as well as on the promotion of peaceful uses of nuclear energy. The thesis contributes to the advancement of knowledge and understanding of the corrosion mechanisms and interactions between SiC and liquid metal, which are crucial for the design and operation of the DFR. The thesis also proposes a micro demonstrator loop facility, which aims to conduct corrosion tests on SiC samples under realistic conditions, which can provide valuable experimental data and validation for the DFR. These are undoubtedly important studies that can be used to decide on the future use of nuclear reactors in Poland and other countries.

The main new and original contribution of this thesis is this is the first study to investigate the corrosion of 3C-SiC by liquid lead using density functional theory (DFT) and molecular dynamics (MD) simulations, revealing the adsorption energies, charge density differences, band structures, partial density of states, diffusion coefficients, and activation energies of different crystal planes and coverages. It provides valuable insights and data for the design and operation of the DFR technology, which is a novel concept of a fast nuclear reactor that uses liquid metal fuel and coolant, offering advantages such as high efficiency, fuel breeding, waste reduction, and passive safety features. The implementation of such methodology in terms of sophistication, accuracy, and completeness has also not been presented in the subject literature so far. The performed analyses by comparing the obtained numerical results with the data of experimental measurements contributed to the validation of the applied computational code, which is a critical issue in the simulation and operation of nuclear facilities.

The work is 74 pages long and consists of 6 chapters, a reference chapter, and no appendices. At the beginning of the work, the author has included a table of contents, a list of figures and an abstract with a summary of the work. At the end of the work, there is a bibliography and no appendices. The thesis contains 27 figures, but, surprisingly, it does not contain any tables. The figures contain summaries of the research results and are of appropriate quality for a PhD thesis. The bibliography consists of 166 literature items, on a wide range of relevant topics. The bibliography includes both older works documenting the basics of the methods used, and recently published works representing the current state of knowledge, which shows the author's good orientation in the research topic. The outline of the thesis describes the main parts of the dissertation, which include a theoretical background of the DFR technology and the selected materials, a review of the corrosion mechanisms and mitigation methods, a presentation of the simulation results and a summary of the findings.

Chapter 1 is an introduction and introduction to the topic, which is high-temperature corrosion of ceramic construction materials for the Dual Fluid Reactor. The author is motivated by the challenges and opportunities of the DFR reactor, which uses novel materials and operates at high temperatures and pressures. The author aims to study the corrosion behavior of materials in DFR reactor environment. The objective of the thesis is to determine the most corrosion-resistant surface of the 3C-SiC crystal, which is a structural material for the DFR reactor, using DFT and MD simulations. The author also aims to design an experimental loop for testing the corrosion resistance of different materials. The research hypothesis is that the (111) surface of the 3C-SiC crystal is more stable than the (100) and (110) surfaces in contact with lead, which is the coolant for the DFR reactor. The author also expects that the SiC/SiC composite is suitable for use in the DFR reactor. These main objectives have been fully met in the remainder of the thesis.

In Chapter 2 of the thesis, the author introduces the Dual Fluid Reactor (DFR) concept, which uses liquid metal fuel and lead coolant in separate loops. The author explains the advantages and challenges of this design, such as high efficiency, fuel breeding, waste reduction, and material selection. The author reviews the properties and production methods of silicon carbide (SiC), which is the chosen structural material for the DFR. The author discusses the different forms and grades of SiC, such as 3C-SiC, SiC/SiC composites, and CVD SiC, and different manufacturing methods. The author describes the characteristics and benefits of lead as the coolant material for the DFR, which is its high thermal conductivity, low neutron capture, high radiation shielding, and low chemical reactivity of lead. The author then presents the composition and properties of the metallic fuel for the DFR, which is a eutectic mixture of uranium and chromium. Its benefits are lower melting point, increased thermal conductivity, and improved neutron economy of the fuel. The methods and materials discussed here, along with their advantages and disadvantages, provide the basis and motivation for proposing improvements and developments.

Chapter 3 is devoted to the various mechanisms and factors that affect the corrosion of ceramic materials by liquid metal, especially lead, which is the coolant for the DFR reactor. The author considers the dissolution, reaction, diffusion, erosion, and radiation effects of lead on different types of ceramics, such as SiC, Si3N4, AIN, AI4C3, BN, and others. It includes extensive review of the oxidation behavior of ceramic materials in the presence of oxygen and other impurities, such as water vapor and molten salts. The author explains how the formation and stability of oxide layers, such as SiO2, AI2O3, and B2O3, influence the corrosion resistance and mechanical properties of ceramics, and interactions of ceramic materials with uranium and chromium, which are the components of the metallic fuel for the DFR reactor. The author shows how these metals can dissolve in or react with ceramics, forming carbides and silicides that can either enhance or degrade the surface condition of ceramics. The author presents methods to limit the corrosion effects of ceramic materials in the DFR reactor, such as selecting the proper production method, pre-oxidizing, or pre-alloying the surface, controlling the oxygen concentration and temperature, and cleaning the circuits. The author correctly identifies the main issues associated with corrosion. Being aware of the limitations of the current methods, the author took on the challenge of developing and improving methods of calculating the material interaction, which he described, implemented, demonstrated, and validated in his doctoral thesis.

The Chapter 4 discusses the topic of molecular dynamics (MD) simulations to study the time-dependent behavior of atomistic systems, such as the interactions of lead with different surfaces and the diffusion of lead in the crystal and the amorphous form of silicon carbide and silicon oxide. The author employs the LAMMPS software and the Tersoff and Lennard-Jones potentials to define the interatomic forces and solve Newton's equations of motion for each atom. The author also uses the Verlet algorithm, the NPT and NVT ensembles, and the Nosé-Hoover thermostat and barostat to control the temperature and pressure of the system. The author presents the results of the simulations for seven representative surfaces: (100), (110), and (111) with C-face or Si-face termination. The thesis compares the results with the previous DFT calculations and finds some discrepancies due to the limitations of Lennard-Jones potential. It is observed that carbon atoms tend to migrate to the surface and form an amorphous layer that limits further diffusion. The author calculates the diffusion coefficient of lead in silicon carbide at different temperatures and the mean square displacement method. The author finds that the diffusion rate increases with temperature and is higher in the amorphous form than in the crystalline form. The author also estimates the activation energy and the diffusion using the Arrhenius equation. The results suggest a diffusion-driven corrosion mechanism. The main part of the dissertation is devoted to developing a computational method for SiC corrosion in DFR reactor. This is a major and time-consuming challenge, which was undertaken by the author and described in this chapter, and the main achievement is detailed here, which is an original achievement of this work worthy of a doctorate.

Chapter 5 is devoted to description of the design and objectives of a micro-demonstrator (µD) loop, which is a double-loop experiment that uses liquid lead as both fuel and coolant. The µD loop is a prototype for a more advanced mini-demonstrator (mD) loop that will simulate the DFR reactor conditions more closely. The author explains the main components and functions of the µD loop, such as the main tank, the heat exchanger, the expansion tanks, the radiator, the pumping system, the sensors, and the oxygen measurements and control system. The author presents the corrosion experiment details, which involve mounting samples of silicon carbide and steel on different points along the pipes and measuring their corrosion behavior over time. The author also plans to incorporate irradiated samples to study the radiation effects on corrosion. The author analyzes and discusses the results and challenges of the µD loop project, which serves as a milestone for developing the DFR reactor technology. This is a significant contribution to the state of the art, and the study is unified and transparent.

Chapter 6 contains a summary and conclusions drawn from the calculations, especially on the applicability of the new method to a nuclear power reactor. The author also discusses the limitations and challenges of the thesis, such as the lack of experimental validation for the simulation results, the uncertainty of the oxygen concentration and temperature ranges, and the difficulty of obtaining high-quality samples and coatings. The author suggests future directions and improvements for the research, such as conducting long-term corrosion tests in realistic reactor conditions, studying the effects of irradiation and flow on corrosion, developing advanced sensors and pumps for the loop, and exploring other potential materials and coatings.

Chapters 3, 4 and 5 are the most important chapters of the work and form the core of the author's scientific output. The results obtained are undoubtedly crucial for the further development and experimental validation of codes for simulating nuclear installations. The work is written clearly, the reasoning is presented clearly and consistently. The purpose of the work and the research problems posed are clearly defined, and the methods and algorithms used are precisely described. The results obtained are illustrated with adequate figures and tables. The thesis proposed by the author, discussed in Chapter 1, has been proven and fulfilled in this work. Certainly, the doctoral student has met the stated objectives, in particular:

- It provides a comprehensive overview of the DFR technology and its advantages over other reactor types, and the selected materials, such as 3C-SiC, SiC/SiC composites, and metallic fuel.
- It analyzes the chemical interactions and corrosion mechanisms of SiC, the structural material, with lead, the coolant, and fuel carrier, at high temperatures.
- It performs DFT and MD simulations to study the surface structure and stability of different crystal planes of 3C-SiC in contact with lead atoms.
- It describes the design and operation of a micro-demonstrator loop facility for corrosion testing and validation of simulation results.
- It proposes ways to mitigate corrosion effects, such as pre-oxidation, doping, and protective coatings.

The common, unifying goal of all the topics described in this thesis is to investigate the feasibility and challenges of using SiC as a structural material for the Dual Fluid Reactor technology, which employs a liquid metal fuel and a lead coolant. Specifically, to explore the corrosion mechanisms and mitigation methods of SiC in contact with lead at high temperatures, using both experimental and computational approaches.

I have the following main criticisms of the work:

- The thesis does not perform any experimental validation of the simulation results, which may limit the reliability and applicability of the findings.
- The thesis uses a simple Lennard-Jones pair potential to describe the interactions with lead, which may not be accurate enough for dense and bonded substances. The thesis acknowledges this limitation but does not explore other alternatives or compare with existing data.

The perceived weaknesses and inaccuracies mentioned above do not in any way detract from the merits of the work. I would like to emphasize that the dissertation demonstrates the versatility of the candidate's interests and skills and addresses many issues concerning the calculation of the material behavior in corrosive environment.

In my opinion, the dissertation meets all the customary and legal requirements for a doctoral thesis, which are necessary to receive a doctoral degree. Accordingly, I request that Mr. Michał Komorowicz be admitted to the public defense and further stages of the doctoral dissertation.

Brent Jeffery Heuser

Brent J. Heuser

UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN

217.333.2295 • (f) 217.333.2906 • nuclear@illinois.edu • npre.illinois.edu