

Editorial

Special Issue: Behavior of Materials (Alloys, Coatings) in Conditions Specific to Gen IV Nuclear Reactors

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Today, countries all over the world, faced with a global energy crisis and the effects of climate change, are looking for alternatives to fossil fuels. Thus, there is a renewed interest in nuclear energy, considered a much cleaner alternative with significantly lower carbon emissions. Given the global situation, an international cooperative alliance was created in 2001 to study the practicality and performance of Generation IV (GEN IV) reactors to ensure a global, safe, innovative, sustainable and economic energy source [1]. This international alliance—the Generation IV International Forum or GIF—selected six emerging nuclear technologies are classified by their cooling agents as follows: gas-cooled reactors (GFR and VHTR), molten metal-cooled reactors (LFR), molten salt reactors (MSR), sodium-cooled reactors (SFR) and supercritical water-cooled reactors (SCWR) [1]. They believed that these innovative nuclear reactors can guarantee the low-carbon, long-term, safe and economical production of energy.

Since these nuclear systems use very harsh coolants, the main challenge lies in the identification of suitable structural materials and fuel claddings to withstand the various combinations of high temperatures, high pressures and radiation [2,3]. Although each reactor has its own challenges in terms of structural materials, there are some common issues, such as resistance to uniform and localized corrosion, dimensional stability to creep at high temperatures and resistance to radiation damage [4,5]. To select appropriate materials for nuclear reactor components, many types of commercial alloys (martensitic, austenitic and Ni-based alloys) or newly developed alloys such as oxide dispersion strengthened alloys (ODS), refractory alloys, ceramics, carbides, nitrides, coatings and high entropy alloys have been tested under simulated operating conditions [6]. In the case of the LFR system, structural materials compatible with Pb or Pb–Bi at high operation temperatures (520 °C) are essential, because liquid lead is more damaging to structural steel than other coolants such as helium or sodium [7].

In low-temperature LFR, the main components could be composed of austenitic AISI 316 stainless steel for lower radiation doses, while for high doses, martensitic steels are recommended due to their resistance to void swelling under radiation [8,9]. On the other hand, in high-temperature LFR, refractory metals or ceramics would be more appropriate, but so far there are limited results on the performance of these materials. Thus, to improve the swelling resistance of austenitic steels, the microstructure can be stabilized with appropriate alloying elements [10]. At the same time, anticorrosive barriers, such as Al₂O₃ (or other ceramics), deposited on the metal substrate [11] or the addition of aluminum to the



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alloy composition (the so-called austenitic alumina forming steels) are proven to be very effective in the prevention of corrosion by liquid lead [12,13].

The GFR system is a GEN IV design combining the advantages of gas-cooled high-temperature reactors and a fast neutron spectrum reactor. Helium is used as a coolant, and the outlet temperature of the core is around 850 °C [14]. The main challenge for the structural materials of this reactor vessel will be in its resistance to fast neutron irradiation and high temperatures. Therefore, it is believed that ceramic materials, composite ceramics or intermetallic compounds may be viable in this core [15]. For the fuel claddings of a GFR, operating at temperatures beyond the current capabilities of heat-resistant alloys, advanced refractory materials or SiCf/SiC composites, which maintain their strength and toughness up to very high temperatures, may be employed [16]. For the other core components, coated or uncoated ferritic-martensitic steels, austenitic steels and Fe–Ni–Cr alloys are potential materials, while for the pressure vessel, heat resistant ferritic–martensitic 9%–12% Cr and modified 2 1/4Cr-1Mo steels show promise.

As its name implies, the very high-temperature reactor (VHTR) system is designed to operate at higher temperatures than GFR, which necessitates the use of materials with further enhanced properties for the internal components [17]. It is estimated that the outlet temperature of this type of reactor will be between 950 and 1100 °C, which will require the development of superalloys based on Ni–Cr–W. Graphite with improved structural strength is proposed for the core material, and for the other internal components, ceramic materials such as C–C composites reinforced with fibers, ceramic, sintered SiC or oxide composite ceramics are suggested [18–22].

The same problems with the selection of materials resistant to higher outlet temperatures also exist in the case of the molten salt reactor (MSR). The temperature of the coolant (fluorine salts) is from 700 °C (at very low pressure) up to 800 °C [23]. For MSR systems operating under these conditions, mainly preexisting alloys have been proposed, namely Ni-based alloys, Nb–Ti alloys, modified Hastelloy N and graphite. Graphite can function as both a structural material of the core and the moderator. However, there are challenges associated with the use of graphite, such as dimensional changes induced by irradiation, salt penetration into graphite and absorption of xenon. To date, tests carried out in fluoride salts at temperatures up to 800 °C have proven that modified Hastelloy N is resistant to corrosion under these harsh conditions [23]. Additionally, nickel-based alloys have proven to be suitable structural materials for MSRs due to their strong, stable, corrosion resistant and good welding characteristics.

Another proposed reactor is the sodium-cooled reactor system, which will have an outlet temperature of 550 °C, requiring the use of alloys resistant to high temperatures and a sodium environment, for example, alloys hardened by oxide dispersion (ODS). Another material proven to be resistant to high temperatures and creep in sodium environments is ferritic steel with 12% Cr [24].

The supercritical water-cooled reactor (SCWR) is a promising Gen IV design, as it offers an enhanced thermal efficiency in comparison to light water reactor (LWR) technologies currently in operation. In addition, the abundant experience gained from PWR, BWR and supercritical fossil plant operation can be exploited in the development of this system [25]. Despite the promised advantages, a high pressure (25 MPa) and high temperatures (up to 620 °C) lead to changes in the physicochemical properties of water, which in combination with radiation becomes a harsh environment for SCWR component materials. Therefore, research carried out in this field aims to combat general corrosion; testing stress corrosion cracking of different non-irradiated and irradiated alloys. The evaluation of the effect of radiolysis and the establishment of water chemistry are also interesting research areas in this field. Additionally, through tests under simulated operating conditions, it was possible to evaluate the dimensional and microstructural stability, strength, embrittlement, creep resistance of the candidate alloys and perform thermo-hydraulic analyzes of the SCWR [26]. The alloys proposed as candidate materials for SCWRs are commercial alloys such as austenitic steels (series 3xx), nickel-based alloys, ferritic-martensitic alloys and ODS alloys

with a ferritic or austenitic structure. On the other hand, to improve the corrosion resistance of the materials used in the internal components of the reactor, coatings (e.g., CrN and NiCrAlY) are proposed as possible solutions [27]. Future research should be targeted to fill existing gaps in the knowledge, with a precise focus on materials used in the temperature range of 280–620 °C and in the irradiation dose ranges of 10–30 displacements per atom (dpa) (thermal spectrum) and 100–150 dpa (fast spectrum) [28]. GIF meet bi-annually to review the status of SCWR project plans, report on the research and development activities—including benchmarking exercises and interlaboratory projects—and engage with international collaborators. For example, the ECC-SMART project [29] connects research institutes from Europe, Canada and China to develop supercritical water-cooled small and modular reactors. The main objective of this collaboration is to identify the design requirements for this technology and to establish the pre-licensing and guidelines to ensure the safety of further technological developments.

Following the analyses carried out, only a few classes of materials described have the potential to support the operating conditions of Generation IV nuclear reactors. Regardless of the type of coolant in these systems, austenitic steels are suitable structural materials. In addition, ceramics such as SiCf/SiC composites [30], Cf/C composites and alumina protective coatings [30] may be attractive due to their proven high temperature stability and resistance to wear, corrosion and erosion. Thus, materials such as aluminosilicates, Al₂O₃, TiO₂, ZrC, ZrN, ZrxSiy, B₄C, WC, graphite and graphene are being explored for their abilities to form surface modifications, surface coatings or alloys to improve the corrosion resistance of ferritic martensitic steels. Surface coating technology presents another solution to improve the corrosion resistance of candidate materials for next-generation nuclear systems through various different methods [31]. Additionally, the ferritic alloy FeCrAl has been intensively studied as an excellent substitute for zircaloy claddings [32,33]. The modification of this material by oxide dispersion, forming so-called ODS-FeCrAl, may be of interest in nuclear applications due to its resistance to irradiation, creep and corrosion [34]. Last but not least, it is believed that new fission reactors require the use a new class of alloys altogether, with exceptional properties beyond those of conventional alloys, leading to the development of high entropy alloys (HEAs) [35].

The development of nuclear technologies still faces challenges and continuing materials research is crucial in order to find appropriate solutions.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. DoE, U.S. A Technology Roadmap for Generation IV Nuclear Energy Systems. In *Proceedings of the Nuclear Energy Research Advisory Committee and the Generation IV International Forum*; 2022. Available online: https://www.gen-4.org/gif/jcms/c_40481/technology-roadmap (accessed on 4 November 2022).
2. Murty, K.L.; Charit, I. Structural materials for Gen-IV nuclear reactors: Challenges and opportunities. *J. Nucl. Mater.* **2008**, *383*, 189–195. [CrossRef]
3. Yvon, P. *Structural Materials for Generation IV Nuclear Reactors*, 1st ed.; Woodhead Publishing: Sawston, UK, 2016; ISBN 9780081009062.
4. Allen, T.R.; Sridharan, K.; Tan, L.; Windes, W.E.; Cole, J.I.; Crawford, D.C.; Was, G.S. Materials Challenges for Generation IV Nuclear Energy Systems. *Nucl. Technol.* **2008**, *162*, 342–357. [CrossRef]
5. Zinkle, S.J.; Was, G.S. Materials challenges in nuclear energy. *Acta Mater.* **2013**, *61*, 735–758. [CrossRef]
6. Hosemann, P.; Vujić, J. Material issues for current and advanced designs. *Contemp. Mater.* **2014**, *5*, 10–25. [CrossRef]
7. Tarantino, M.; Angiolini, M.; Bassini, S.; Cataldo, S.; Ciantelli, C.; Cristalli, C.; Del Nevo, A.; Di Piazza, I.; Diamanti, D.; Eboli, M.; et al. Overview on Lead-Cooled Fast Reactor Design and Related Technologies Development in ENEA. *Energies* **2021**, *14*, 5157. [CrossRef]
8. Vogt, J.-B.; Proriot Serre, I. A Review of the Surface Modifications for Corrosion Mitigation of Steels in Lead and LBE. *Coatings* **2021**, *11*, 53. [CrossRef]
9. Fazio, C.; Balbaud, F. Corrosion phenomena induced by liquid metals in Generation IV reactors. In *Structural Materials for Generation IV Nuclear Reactors*; Elsevier: Amsterdam, The Netherlands, 2017; pp. 23–74.

10. Nuclear Energy Agency (NEA). Nuclear Energy Agency, Corrosion protection in lead and lead-bismuth eutectic at elevated temperatures. In *Handbook on Lead-Bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal-hydraulics and Technologies*; 2015; pp. 631–632. Available online: https://inis.iaea.org/collection/NCLCollectionStore/_Public/46/133/46133907.pdf (accessed on 5 November 2022).
11. Chen, Y.; Hu, L.; Qiu, C.; He, B.; Zhou, J.; Zhao, J.; Li, Y. Influence of LBE Temperatures on the microstructure and properties of crystalline and amorphous multiphase ceramic coatings. *Coatings* **2019**, *9*, 543. [\[CrossRef\]](#)
12. Yamamoto, Y.; Brady, M.P.; Lu, Z.P.; Maziasz, P.J.; Liu, C.T.; Pint, B.A.; More, K.L.; Meyer, H.M.; Payzant, E.A. Creep-resistant Al₂O₃-forming austenitic stainless steels. *Science* **2007**, *316*, 433–436. [\[CrossRef\]](#)
13. Ejenstam, J.; Szakalos, P. Long term corrosion resistance of alumina forming austenitic stainless steels in liquid lead. *J. Nucl. Mater.* **2015**, *461*, 164–170. [\[CrossRef\]](#)
14. Čížek, J.; Kalivodová, J.; Janecek, M.; Stráský, J.; Srba, O.; Macková, A. Advanced Structural Materials for Gas-Cooled Fast Reactors—A Review. *Metals* **2021**, *11*, 76. [\[CrossRef\]](#)
15. Zinkle, S.J. Nuclear technology applications of ceramics, composites and other nonmetallic materials. In Proceedings of the IAEA/ICTP School on Physics of Radiation Effects and its Simulation for Non-Metallic Condensed Matter, Trieste, Italy, 13–24 August 2012.
16. Steinbrück, M.; Angelici, A.V.; Markel, I.J.; Stegmaier, U.; Gerhards, U.; Seifert, H.J. Oxidation of SiCf-SiC CMC cladding tubes for GFR application in impure helium atmosphere and materials interactions with tantalum liner at high temperatures up to 1600 °C. *J. Nucl. Mater.* **2019**, *517*, 337–348. [\[CrossRef\]](#)
17. Corwin, W.R.; Burchell, T.D.; Katoh, Y.; McGreevy, T.E.; Nanstad, R.K.; Ren, W.; Snead, L.L.; Wilson, D.F. *Generation IV Reactors Integrated Materials Technology Program Plan: Focus on Very High Temperature Reactor Materials*; Oak Ridge National Lab.: Oak Ridge, TN, USA, 2008.
18. Park, J.Y. SiCf/SiC composites as core materials for Generation IV nuclear reactors. In *Structural Materials for Generation IV Nuclear Reactors*; Chapter 12; Yvon, P., Ed.; Elsevier Ltd.: Amsterdam, The Netherlands, 2017; pp. 441–470.
19. Katoh, Y.; Snead, L.L.; Henager, C.H., Jr.; Nozawa, T.; Hinoki, T.; Ivekovic, A.; Novak, S.; Gonzalez de Vicente, S.M. Current status and recent research achievements in SiC/SiC composites. *J. Nucl. Mater.* **2014**, *455*, 387–397. [\[CrossRef\]](#)
20. Marsden, B.J.; Jones, A.N.; Hall, G.N.; Treifi, M.; Mummery, P.M. Graphite as a core material for Generation IV nuclear reactors. In *Structural Materials for Generation IV Nuclear Reactors*; Chapter 14; Yvon, P., Ed.; Elsevier Ltd.: Amsterdam, The Netherlands, 2017; pp. 495–532.
21. Zhou, X.W.; Tang, Y.P.; Lu, Z.M.; Zhang, J.; Liu, B. Nuclear graphite for high temperature gas-cooled reactors. *New Carbon Mater.* **2017**, *32*, 193–204. [\[CrossRef\]](#)
22. Weaver, K.D.; Totemeier, T.; Feldman, E.E.; Kulak, R.F.; Tzanos, C.P.; Cheng, L.-Y.; Jo, J.; Corwin, W.; Gale, W.F.; Allen, T.; et al. Gas-Cooled Fast Reactor (GFR) FY 05 Annual Report; Idaho National Laboratory Report INL/EXT-05-00799; 2005. Available online: <https://inldigitallibrary.inl.gov/sites/sti/sti/3480236.pdf> (accessed on 5 November 2022).
23. Guo, S.; Zhang, J.; Wu, W.; Zhou, W. Corrosion in the molten fluoride and chloride salts and materials development for nuclear applications. *Prog. Mater. Sci.* **2018**, *97*, 448–487. [\[CrossRef\]](#)
24. Chengliang, L.; Mengjia, Y. The Challenge of Nuclear Reactor Structural Materials for Generation IV Nuclear Energy Systems. In Proceedings of the 20th International Conference on Structural Mechanics in Reactor Technology (SMiRT 20), Espoo, Finland, 9–14 August 2009. SMiRT 20-Division 10, Paper 1586.
25. Guzonas, D.; Novotny, R. Supercritical water-cooled reactor materials e Summary of research and open issues. *Progress in Nuclear Energy* **2014**, *77*, 361–372. [\[CrossRef\]](#)
26. Buongiorno, J.; MacDonald, P.E. Supercritical Water Reactor (SCWR)—Progress Report for the FY-03 Generation-IV R&D Activities for the Development of the SCWR in the U.S.; 2003. Available online: <http://large.stanford.edu/courses/2017/ph241/jones-c1/docs/ext-03-01210.pdf> (accessed on 5 November 2022).
27. Nieuwenhove, R. Van Investigation of coatings, applied by PVD, for the corrosion protection of materials in supercritical water. In Proceedings of the 6th International Conference on Supercritical Water Reactors, Shenzhen, China, 3 March 2013.
28. Baidur, S. Materials challenges for the Supercritical Water-Cooled Reactor (SCWR). *Can. Nucl. Soc. Bull.* **2008**, *29*, 32–38.
29. Joint European Canadian Chinese Development of Small Modular Reactor Technology. Available online: <https://ecc-smart.eu/> (accessed on 5 November 2022).
30. Yutai, K.; Lance, S. Silicon carbide and its composites for nuclear applications-historical overview. *J. Nucl. Mater.* **2019**, *526*, 151849. [\[CrossRef\]](#)
31. Malerba, L.; Al Mazouzi, A.; Bertolus, M.; Cologna, M.; Efsing, P.; Jianu, A.; Kinnunen, P.; Nilsson, K.F.; Rabung, M.; Tarantino, M. Materials for Sustainable Nuclear Energy: A European Strategic Research and Innovation Agenda for All Reactor Generations, Review. *Energies* **2022**, *15*, 1845. [\[CrossRef\]](#)
32. Rebak, R.B.; Terrani, K.A.; Fawcett, R.M. FeCrAl Alloys for Accident Tolerant Fuel Cladding in Light Water Reactors. In Proceedings of the Pressure Vessels and Piping Conference, Vancouver, BC, Canada, 17–21 July 2016. Paper No: PVP2016-63162, V06BT06A009.
33. Huang, X.; Li, X.; Fang, X.; Xiong, Z.; Peng, Y.; Wie, L. Research progress in FeCrAl alloys for accident-tolerant fuel cladding. *J. Mater. Eng.* **2020**, *48*, 19–33.

34. Pint, B.A.; Dryepondt, S.; Unocic, K.A.; Hoelzer, D.T. Development of ODS FeCrAl for Compatibility in Fusion and Fission Energy Applications. *JOM* **2014**, *66*, 2458–2466. [[CrossRef](#)]
35. Miracle, D.B.; Senkov, O.N. A critical review of high entropy alloys and related concepts. *Acta Mater.* **2017**, *122*, 448–511. [[CrossRef](#)]

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