2015 International Nuclear Atlantic Conference - INAC 2015
São Paulo, SP, Brazil, October 4-9, 2015
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-06-9

THE QUEST FOR SAFE AND RELIABLE FUEL CLADDING MATERIALS

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ABSTRACT

The tragic Fukushima Daiichi Nuclear Plant accident of March, 2011, has brought great unrest and challenge to the nuclear industry, which, in collaboration with universities and nuclear research institutes, is making great efforts to improve the safety in nuclear reactors developing accident tolerant fuels (ATF). This involves the study of different materials to be applied as cladding and, also, the improvement in the fuel properties in order to enhance the fuel performance and safety, specifically under accident conditions. Related to the cladding, iron based alloys and silicon carbide (SiC) materials have been studied as a good alternative. In the case of austenitic stainless steel, there is the advantage that the austenitic stainless steel 304 was used as cladding material in the first PWR (Pressurized Water Reactor) registering a good performance. Then, alternated cladding materials such as iron based alloys (304, 310, 316, 347) should be used to replace the zirconium-based alloys in order to improve safety. In this paper, these cladding materials are evaluated in terms of their physical and chemical properties; among them, strength and creep resistance, thermal conductivity, thermal stability and corrosion resistance. Additionally, these properties are compared with those of conventional zirconium-based alloys, the most used material in actual PWR, to assess the advantages and disadvantages of each material concerning to fuel performance and safety contribution.

1. INTRODUCTION

Fuels that present enhanced accident tolerance are those that, in comparison with the standard UO_2–Zircaloy system currently used by the nuclear industry, can tolerate loss of active cooling in the reactor core for a considerably longer time period (depending on the LWR system and accident scenario) while maintaining or improving the fuel performance during normal operations, operational transients, as well as design-basis and beyond design-basis events [1]. Also, it is important to consider in the development of ATF the minimizing of waste generation and of the economic impact.

The demand for ATF became essential for the future of nuclear energy after the tragic Fukushima Daiichi Nuclear Plant accident of March, 2011, which have shown a great susceptibility of zirconium-based alloys cladding in a LOCA event in which the oxidation of zirconium at high temperature produced high amount of hydrogen leading to core melting and explosion of the reactor building [2, 3]. This event brought great concern and challenge to the nuclear power generation industry, universities and nuclear research institutes to improve the existing and future nuclear reactors for more safety and to enhance accident tolerance. In this sense, the cladding material plays an important role since it is the most sensible structural component of a reactor, consisting of the second barrier to avoiding that fuel and fission products can reach the primary coolant circuit.

Chemical compatibility with other reactor core components, melting temperature, thermal conductivity, thermal neutron cross section, manufacturability, gas retention and radiation performance, are the most important fuel and cladding material properties to be considered in order to enhance accident tolerance fuels (ATF) [4].

To improve corrosion resistance, mechanical and physical properties on the original cladding materials, including zirconium-based alloys and stainless steels, select alloying elements (Sn, Nb, Cr, Ni, Fe, Ti, Ta and Co) are used, and that also requires improvements in metallurgical structure and manufacturing processes.

Besides of the exclusively metallic materials nowadays used as cladding, it has been studied in the framework of ATF development, the addition of ceramic sleeves and also, the complete replacement of the conventional cladding material by fully ceramic materials.

In this paper a short outline of the early and current research and development activities on alternative cladding materials, such as, austenitic stainless steel 304, 310, 316, 347, FeCrAl and ceramic to replace zirconium-based alloys is presented. These cladding materials will be evaluated in their physical and chemical properties; among them, strength and creep resistance, thermal conductivity and thermal stability and corrosion resistance. Additionally, these properties will be compared with those of Zircaloy-4, the most used material in actual pressurized water reactors (PWR).

2. CLADDING MATERIALS

This section presents a short description of cladding materials which can be applied in PWR, starting from the conventional zirconium-based alloys.

2.1. Zirconium-based alloys

For some decades zirconium-based cladding had the monopoly in nuclear reactors over other cladding options, such as stainless steel, mainly due to its lower absorption cross section for thermal neutrons, and the successful zirconium-based alloys manufacturing technology.

After decades of research and development, the current zirconium-based alloys, such as ZIRLO^{TM} and M5^{TM}, exhibit optimized behavior in reactor under normal operating conditions, but on accident conditions, this material will still be able to experience severe degradation by rapid oxidation of zirconium at temperature greater than 1200^{o} C [5]. Another important limiting factor for zirconium-based alloys is the powerful oxidation environment provided by the coolant in the primary circuit that influences the oxidation rate and limit the lifetime of reactor materials.

The improvement of the zirconium-based alloys was achieved by means of changes in the alloy composition, as shown in Table 1. In this sense, the reducing in the tin content improved the corrosion resistance of the material. Nonetheless, it was necessary to optimize the tin concentration due to the fact that the presence of lithium in the coolant water increases corrosion at very low tin content [6]. On the other hand, the addition of niobium increased the corrosion resistance and improved the mechanical properties of the material [7].

Table 1: Weight percent composition of different zirconium-based alloys [8]

Alloy	Sn	Nb	Fe	Cr	Ni	Zr
Zircaloy-2	1.3-1.5	--	0.15-0.18	0.10	0.05-0.07	Balance
Zircaloy-4	1.3-1.5	--	0.20	0.10	--	Balance
ZIRLO™	0.67	1.0	0.10	--	--	Balance
M5™	--	1.0	0.04	--	--	Balance

The changes in the chemical composition for the advanced zirconium-based alloys enabled also to reduce the hydrogen pickup while limiting detrimental irradiations effects (grow and creep) compared to the first zirconium-based alloys. Furthermore, since Zircalloy-2, Zircaloy-4 up to ZIRLO™ and M5™ metallurgical enhancements, core operation, zirconium-clad production and water chemistry control have optimized the zirconium-based alloys cladding performance with respect to in-reactor corrosion and hydrogen pickup under normal reactor operational conditions [7]. On the other hand, on accident conditions, zirconium-based alloys are still able to have severe degradation by rapid oxidation of zirconium at temperature greater than 1200^{o} C [4, 5].

2.2. Stainless Steels

In the 1960s, the austenitic stainless steel (AISI) 304 was used as cladding material in the first PWR reactors, however, this material, was replaced by zirconium-based alloys, due to its lower absorption cross section for thermal neutrons, better mechanical and thermal performance over the relatively simple austenitic steels, which were utilized as cladding in the early commercial reactors [9]. Some of these deficiencies were mitigated with the development of the AISI 347 and 348, which present high intergranular corrosion resistance. The low carbon content associated to the addition of tantalum and niobium prevent the corrosion and intergranular precipitation of metallic carbide, M26C6 type, in the region of grain boundaries, avoiding depletion of chromium [10]. The compositions of different AISI types are presented in Table 2.

Table 2: Weight percent composition of different AISI types [11]

AISI	C	Cr	Ni	Mo	Si	Mn	Ta	Co	Fe
304	0.07	17.5-19.5	8-10.5	--	0.75	2.0	--	--	Balance
310	0.25	24-26	19-22	--	1.5	2.0	--	--	Balance
316	0.08	16-18	10-14	2-3	0.75	2.0	--	--	Balance
347	0.08	17-19	9-13	--	0.75	2.0	Nb+Ta 10xCmin./1.0	--	Balance
348	0.08	17-19	9-13	--	0.75	2.0	0.10	0.20	Balance

In the last decades, stainless steels have made significant performance improvements that include corrosion resistance, high-strength and other mechanical and thermal properties with the addition of stabilizing elements, changes in the chemical composition of major or minor elements, modifications in the metallurgical structure as well as greater care in their fabrication conditions through better solution annealing temperature, intermediate heat treatments and cold work rate. The expansion of safety margins under high duty operation were considered to overcome the drawbacks of these materials, and now, a new generations of increasingly higher performance stainless steels are commercial available, and have become potential fuel cladding materials to replace zirconium-based alloys [9].

The Tables 3 and 4 present the mechanical and thermal properties of different AISI types at room temperature, respectively.

Table 3: Mechanical properties of different stainless steels at room temperature [12, 13, 14, 15]

AISI	Yield Strength (MPa)	Ultimate Tensile strength (MPa)	Elongation (%)	Dureza (HB)
304	205	515	40	201
310	205	515	40	217
316	290	580	50	150
347	260	520	40	190
348	275	655	45	165

Table 4: Thermal properties of austenitic stainless steels [15, 16]

AISI	Melting Point (K)	Thermal Conductivity ($W\ m^{-1}K^{-1}$)	Resistivity (µOhm cm)	Expansion ($10^{-6}\ K^{-1}$)
304	1450	16.3	72	16.6
310	1450	14.2	72	16
316	1427	15.9	74	16-18
347	1425	16.3	75	16-18
348	1400	19.1	79	18.5

The data presented in Tables 3 and 4 show that in terms of mechanical and thermal properties all studied types of AISI present similar behavior. The main difference is related to the presence of niobium and tantalum in the AIS 348 what improves its corrosion resistance. Data from early PWR that operated for a period using annealed 348 as cladding confirmed its good performance under irradiation [17].

2.3 FeCrAl Alloys

FeCrAl alloys with its chemical composition (wt%), Fe-75, Cr-20, Al 5.0 and a capture cross-section of 2.43 barns [4], is being considered a possible ATF cladding material due to its very low oxidation rate in accident situation that offer several advantages relative to zirconium-based alloys in a PWR environment [5]. However, in most of these alloys creep resistance decreases drastically above 550^o C, and this is a dramatic drawback and the reason why they were not selected for cladding [18], specifically considering accident scenarios.

The properties associated to the FeCrAl alloys become them more appropriate to be used as cladding material in lead-cooled reactors instead of PWR. Lead-cooled reactors work in temperatures lower than 500^{o}C, condition that a thin protective alumina layer is formed reducing the corrosion issue that liquid lead invokes [19].

2.4 Silicon Carbide

SiC-based cladding for nuclear fuel present the advantage of keep its strength and do not creep up to 1300^{o}C, besides of this, the material has been shown to be stable to extremely high irradiation doses and has an important neutronic benefit, as SiC materials parasitically captures fewer neutrons than zirconium-based alloys [4]. According to accident scenarios, the SiC will react more slowly than Zircaloy with steam.

There are different SiC materials which can be applied as cladding in nuclear reactors. One of them is the SiC ceramic matrix composites (CMCs). In this material, the brittle nature of monolithic SiC is mitigated while its structural strength is enhanced by means of the addition of very fine filaments that are combined into fiber tow which are then woven or braided into a tubular cladding. It can be obtained by different processes, which need to be extremely controlled in order to assure that the desired crystalline phase was obtained and to achieve a Si/C ratio equal to 1, since variations in this ratio can affect the properties of the material [20].

There is also the SiC/SiC cladding which is composed by a layer-pair consisting of a SiC CMC outer layer for strength and a dense monolithic β-SiC inner layer for impermeability. Due to the structure of this material that contains porosity and interfaces, the manufacturing process need to be adjust aiming do not compromise the thermal conductivity of the final product.

The SiC Triplex cladding involves the use of a multilayered (monolithic SiC inner layer, SiC CMC middle layer and outer barrier of SiC deposited by chemical vapor deposition) ceramic system to improve the hermeticity to retain fission gas and provide a more ductile behavior [20]. Also in this case, the complexity of the manufacturing process is an important challenge aiming to assure the tolerances in the geometry of the cladding and the uniformity of the properties in the final material.

There is also the possibility of using a hybrid cladding formed by an inner tube of zirconium-based regular alloy wrap by a braided SiC CMC tube. This system presents the advantages that the hermetic seal for the fuel rod is provided by the inner metal liner and the metal end caps is welded to the inner metal liner using traditional sealing processes [20].

The ability to hermetically seal ceramic cladding tubes after the fuel is loaded combined to the development of large scale manufacturing processes that ensures the uniformity of geometry and properties in the final cladding are the major challenges of ceramic materials [4]. Other important point to be considered in order to use these materials in a PWR environment is the amount of residues that can be produced during irradiation and the consequences of that for the coolant system.

3. COMPARISON BETWEEN ZIRCALOY-4 AND AISI 348

Considering the properties and behavior of the discussed materials presented in Section 2, it is evident that stainless steel presents, at the moment, the higher capability to replace zirconium-based alloys as cladding in ATF. One important point is that it was already applied as cladding and the results were good [4].

Among the studied AISI types, the presented data show that the mechanical and thermal properties of 348 are representative of these steels, then it will be used to compare with the equivalent features of Zircaloy-4.

Table 5: Comparative mechanical and thermal properties of Zircaloy-4 and AISI 348 [10]

Property (unity)	Zircaloy-4	AISI 348
Crystalline Structure	HCP	CFC
Ultimate Strength (MPa)	413	655
Tens. St. at Yield (MPa)	241	275
Maximum Elongation (%)	20	45
Elastic Modulus (GPa)	99.3	195
Resistivity (µOhm cm)	74	79
Thermal Conductivity ($Wm^{-1}K^{-1}$)	16.8	19.1
Thermal Expansion Coefficient (10^{-6} K^{-1})	6.7	18.5
Melting Point (^oC)	1825	1400
Under Irradiation Creep (%)	0.3	0.045 ($\varphi t = 3.10^{21}$ n cm^{-2})
Capture Cross-section (Barn)	0.184	3.13

According to Table 5, AISI 348, at a fluence of $3x10^{21}$ n cm^{-2}, present a total creep of 0.045 %, which is about 7 times less than that of Zircaloy-4. AISI 348 has a thermal expansion coefficient of about three times higher than that of Zircaloy-4, which results in a fuel rod gap larger than in Zircaloy-4. Under steady state operation condition Zircaloy-4 is highly resistant to void swelling, but present a substantial axial growth, but AISI 348 has an isotropic grow and is susceptible to void swelling. The elastic modulus of 348 is higher than Zircaloy-4, which means that the cladding deformation is much smaller than those of Zircaloy-4 cladding. This behavior was confirmed by means of simulations carried out using adapted fuel performance codes to evaluate fuel rods with AISI 348 as cladding and comparing to the performance of Zircaloy-4 under a common power history [10, 21]. The results showed that AISI 348 rods display higher fuel temperatures and wider gaps than Zircaloy-4 rods. No gap closure is observed for AISI 348 while the Zircaloy-4 cladding spends a high fraction of life in a state of tensile stress at the ridge. Nevertheless, the thermal performance of both materials is very similar.

The disadvantages of AISI 348 related to Zircaloy-4 are its lower melting point and higher absorption cross section for thermal neutrons, which is about 17 times smaller than that of

AISI348 [14]. However, this neutron absorption penalty could be compensated combining U-235 enrichment increase with pitch changes without significant economic impact.

4. CONCLUSIONS

After decades of research, zirconium-based alloys cladding performance have improved with respect to in-reactor corrosion and hydrogen pickup under normal reactor operational conditions, but on accident conditions, this material is still able to have severe degradation by rapid oxidation of zirconium at temperature greater than 1200°C, making necessary the developing of ATF.

According to the different aspects discussed in this paper, which considered physical, thermal and mechanical properties, manufacturing processes and behavior under irradiation of materials that could be used as cladding in ATF, the stainless steel, specifically AISI 348, arises as the most promising material in a short time due to the following reasons: it was already used, then tested, as cladding in the first PWR presenting a good performance; its thermal and mechanical properties are in agreement with the requirements concerning to corrosion and creep under irradiation in PWR environment; there are available data concerning to its behavior after irradiation; its manufacturing process nowadays is highly optimized; and it does not present the oxidation at high temperature producing high amount of hydrogen.

The question related to the neutron penalty of stainless steel could be solved with small changes in the design aiming to compensate this problem.

It is important to consider that the use of a completely new cladding material implies in a big effort to develop large scale industrial production and this, depending on the complexity in the manufacturing the process, will increase the cost of the fuel operation what can compromise the use of this materials as cladding.

ACKNOWLEDGMENTS

The authors are grateful to the technical support of CTMSP, IPEN-CNEN/SP and POLI/USP.

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