



Zirconium carbide coating for corium experiments related to water-cooled and sodium-cooled reactors

K. Plevacova^a, C. Journeau^{a,*}, P. Piluso^a, V. Zhdanov^{b,1}, V. Baklanov^b, J. Poirier^c

^a CEA, DEN, STRI, LMA, Cadarache, 3108 St. Paul lez Durance, France

^b IAE, National Nuclear Centre, Material Structure Investigation Dept., Krasnoarmeiskaya, 10, Kurchatov City, Kazakhstan

^c CEMHTI, 1D, av. de la Recherche Scientifique, 45071 Orléans Cedex 2, France

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ABSTRACT

Since the TMI and Chernobyl accidents the risk of nuclear severe accident is intensively studied for existing and future reactors. In case of a core melt-down accident in a nuclear reactor, a complex melt, called corium, forms. To be able to perform experiments with prototypic corium materials at high temperature, a coating which resists to different corium melts related to Generation I and II Water Reactors and Generation IV sodium fast reactor was researched in our experimental platforms both in IAE NNC in Kazakhstan and in CEA in France. Zirconium carbide was selected as protective coating for graphite crucibles used in our induction furnaces: VCG-135 and VITI. The method of coating application, called reactive wetting, was developed. Zirconium carbide revealed to resist well to the $(U_x, Zr_y)O_{2-z}$ water reactor corium. It has also the advantage not to bring new elements to this chemical system. The coating was then tested with sodium fast reactor corium melts containing steel or absorbers. Undesirable interactions were observed between the coating and these materials, leading to the carburization of the corium ingots. Concerning the resistance of the coating to oxide melts without ZrO_2 , the zirconium carbide coating keeps its role of protective barrier with $UO_2-Al_2O_3$ below 2000 °C but does not resist to a $UO_2-Eu_2O_3$ mixture.

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1. Introduction

In order to understand the consequences of a core melt-down accident in a nuclear power plant, large R&D programs are conducted in particular by the Alternative Energies and Atomic Energy Commission (CEA) in France and the Institute of Atomic Energy, National Nuclear Center (IAE NNC RK) in Kazakhstan.

A core melt-down accident might occur for instance in case of a core cooling system failure. Indeed, the loss of coolant flow may lead to a rapid increase in temperature larger than 2500 °C. Consequently, the melting of different materials that compose the nuclear reactor, such as fuel, claddings and structural materials may occur.

The mixture of all these materials, called corium, is very complex and chemically aggressive. In light water reactors of Generations II and III Pressurised Water Reactors (PWR) or Boiling Water Reactors (BWR), the core of the reactors contains principally uranium oxide coming from fuel pellets, zircaloy coming from claddings and stainless steel from internal structures. During the increase in temperature these materials oxidize because of the

presence of water, and melt. They form a molten pool of UO_2 , ZrO_2 , Zr and stainless steel that can reach 2800 °C.

Concerning the future generation IV reactors, the sodium fast reactor (SFR) is the current French reference. Its fuel pellets are made of $(U, Pu)O_2$ and claddings and structures of the core are made of different types of stainless steel. Thus, these two materials constitute the major part of SFR corium. Then, as enhanced safety is a priority for this new generation of nuclear power plants, passive mitigation systems are being studied. Some passive mitigation systems will deliver an absorber material, such as boron carbide B_4C or europium sesquioxide Eu_2O_3 , which is able to absorb neutrons and prevent recriticality. Therefore, in case of a core melt-down accident in SFR, the B_4C (and its cladding) might be mixed with corium.

To be able to perform experiments in the field of nuclear severe accidents, two main solutions are available to contain such complex and diverse corium mixtures. First solution is performing the melting experiments in cold crucibles. This method of direct inductive heating of electrically conductive melts is for example used in COMETA facility (NRI, Czech Republic) [1] for the investigation of phase diagrams of systems containing UO_2 and other refractory oxides. It is also used in corium–steel interaction melt tests in RASPLAV-2 facility (NITI, Russia) [2]. Another solution is the use of hot crucibles, for which a very refractory and chemically stable material is needed. Among refractory materials, metals, oxides or

* Corresponding author.

E-mail address: christophe.journeau@cea.fr (C. Journeau).

¹ Present address: IBRAE, Lavrent'ev Ave., 630090 Novosibirsk, Russia.

carbides can be chosen [3,4]. Refractory metals, molybdenum or tungsten, are for example used in the KROTOS facility (CEA, France) to contain corium [5]. Concerning the refractory oxides, partially stabilised hafnium dioxide was developed to contain corium in VERDON furnace (CEA, France) [6] and magnesium oxide has also been used as liner to contain corium-concrete melts (ANL, USA) [28]. But it is graphite which is one of the most common refractory materials used for hot crucibles in furnaces. It is easily available and can resist to very high temperatures, up to 3650 °C, under neutral or reducing atmosphere. It has also optimum specific electric resistance for induction heating using hot crucibles technique. Nevertheless it is a strong reducer, which creates problems with melts containing oxides such as UO_2 . That is the reason why IAE NNC RK and CEA research a way to protect the graphite crucibles of their induction furnaces.

In this paper, we will first describe the experimental facilities and how the material which resisting to the $(\text{U}_x, \text{Zr}_y)\text{O}_2$ water reactor corium melt was selected. Second, the method of coating application will be presented. Then, a large part of the present study will be dedicated to experiments on the selected coating interaction with water reactor corium and with sodium fast reactor corium compositions. Thermodynamic calculations and phase diagrams will be used to interpret those experimental results.

2. Materials and methods

2.1. Experimental setups

Two experimental setups were used to perform experiments on corium resistant materials. The study began with the water reactor corium in IAE NNC RK in Kazakhstan, within the VCG-135 facility. Then, the study continued within the VITI facility at CEA Cadarache, where the sodium fast reactor corium was considered.

2.1.1. VCG-135 facility

VCG-135 facility is an electric melting furnace with induction heating. A generator of 60 kW and 66 kHz is used. The working chamber of 150 L is hermetic and its walls are water cooled. Small-scale heating experiments up to 3000 °C can be performed on samples weighting less than 150 g. A graphite crucible is used to contain the samples. The subsequent cooling is done via the heat losses in water cooled inductor when the generator is disconnected. The temperature is measured using pyrometers and thermocouples. The experiments can be performed under vacuum or under inert gas up to 5×10^5 Pa. A typical scheme of experimental assembly is shown in Fig. 1.

Continuous recording of temperature of the sample and construction elements, the electric power supplied to inductor, the pressure of the working chamber and the pressure of water in

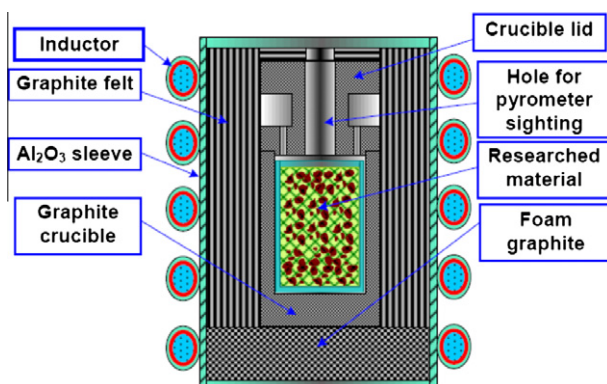


Fig. 1. VCG-135 experimental assembly.

inductance coil can be done by the data acquisition system during the experiments.

2.1.2. VITI facility

VITI (“Viscosity Temperature Installation”) [7,8] facility has been developed to measure viscosity, density and surface tension on corium up to 2600 °C by aerodynamic levitation. But it is also used as small crucibles heating for material interactions tests. This configuration is illustrated in Fig. 2. Samples of less than 100 g can be studied in VITI.

To obtain temperatures up to 2600 °C with limited thermal gradient, induction heating is used. The induction coil is coupled with a graphite susceptor, which heats the crucible by thermal radiation. The radiation losses are attenuated by a special thermal barrier.

The working chamber volume is about 70 L. It is possible to work either under low vacuum or under inert gas. The maximum absolute pressure in the working chamber is 2.5×10^5 Pa. The electrical power of the induction generator is 24 kW and its frequency is 23 kHz.

The temperature of the studied material mixture and the temperature of the external crucible wall are measured by bichromatic pyrometers ($\lambda_1 = 0.92$ and $\lambda_2 = 1.04 \mu\text{m}$).

All experiments within the VITI facility were performed with a 5 L/min argon flow. The absolute pressure of the working chamber was 1.8×10^5 Pa. The samples were heated and then cooled very quickly, about 500 °C/min, when the induction generator was cut.

In the case of a core meltdown accident in a SFR, the corium should be composed of the melted fuel $(\text{U}, \text{Pu})\text{O}_2$, stainless steel coming from melted structures and absorber materials such as the boron carbide B_4C . In the PLINIUS platform, the experiments use the so-called “prototypic corium” in which the $(\text{U}, \text{Pu})\text{O}_2$ fuel is simulated by depleted UO_2 . The use of depleted UO_2 instead of $(\text{U}, \text{Pu})\text{O}_2$ is admissible from the chemical point of view, because the two oxides UO_2 and PuO_2 have relatively similar chemical behaviour.

2.2. Thermodynamic calculations

To simulate possible interactions between the chosen refractory coating and corium, a thermo-chemical equilibria calculation

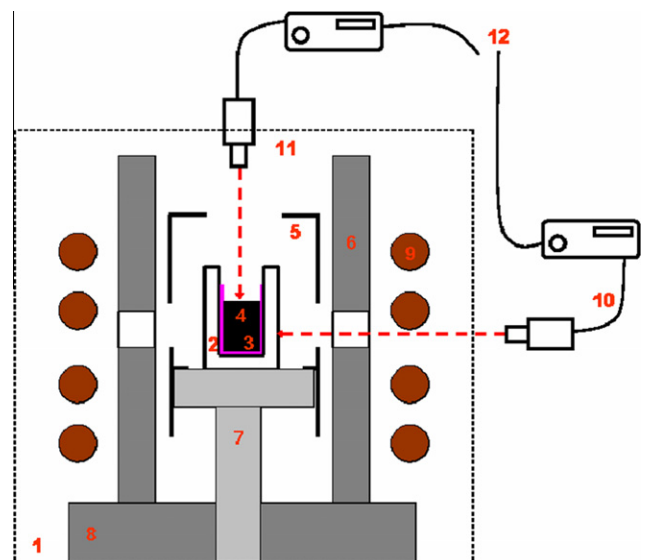


Fig. 2. VITI experimental assembly: (1) VITI chamber, (2) graphite crucible, (3) ZrC -coating, (4) studied mixture, (5) graphite susceptor, (6) thermal shield, (7) support for thermal shield, (8) support for thermal shield, (9) inductance coil, (10) pyrometer – measure of T_{crucible} , (11) pyrometer – measure of T_{mixture} , (12) data acquisition.

software, GEMINI2 (Gibbs Energy MINimizer), was used in this work [9]. This software is based on the principle of minimization of the total Gibbs energy. It is adapted to multicomponent and multiphase chemical systems.

The code is coupled with a thermodynamic database, NUCLEA_08 [10]. This database was developed in the frame of severe accident researches for Pressurised Water Reactors. The main nuclear materials are thus contained in this database.

It is important to underline, that thermodynamic equilibrium is considered for every temperature step in GEMINI2 calculations. The conditions can thus be a little different from experimental conditions.

Then, the calculations are interpolated from the corresponding ternary and binary systems and their thermodynamic properties included in the NUCLEA database. To estimate the reliability of the GEMINI2 results, quality criteria based on comparison between calculation and available experimental data were established for different chemical systems. The quality criteria for binary and ternary sub-systems included in water reactor corium are in general considered as “acceptable”. That means that these systems are well known and satisfactorily modelled. Concerning the sodium fast reactor corium, the quality criteria for several systems containing B_4C are considered as “perfectible”. That means that some domains need complementary experimental data. Nevertheless we showed in [11] that GEMINI2 + NUCLEA_08 are reliable for the U–B–C–O system.

3. Selection of a corium resistant material

3.1. Selection of zirconium carbide such as corium resistant material

The selection of the corium resistant material was done in IAE NNC RK. Indeed, the used experimental setup VCG-135 is an induction furnace made essentially of graphite elements. Thus, a way to prevent the graphite crucible–corium interaction had to be found. The following variants of protection against undesirable interaction were researched: refractory metals inserts in graphite crucibles and refractory materials coatings on the inner walls of the graphite crucible [12]. Series of small-scale experiments were performed to study the chemical resistance of the listed ways. The experiments were performed in model crucibles, which contained about 100 g of corium. The chosen corium was representative of the combination of core materials of pressurized water reactors and boiling water reactors. The use of metallic tantalum or tungsten inserts revealed not to be reliable enough because of their interaction with carbon during the heating until 2600 °C. As a result of this interaction, the metal inserts get deformed and then partially destructed. Carbide coatings revealed to be good candidates for graphite crucible protection. For instance the combined NbC + TaC coating revealed to be efficient as protective barrier for graphite crucibles. But fine dispersed particles of protective TaC-coating have been found in the solidified corium after short time interaction with the corium melt at high temperature.

In some experiments on water reactor core melt components, where the inner walls of the graphite crucible were not previously protected, the graphite crucible wall erosion did not take place. Such unexpected effect was observed in case of increased metal zirconium content, above 12 wt.%, in the corium (Fig. 3a). This effect practically did not depend on the way the zirconium was loaded in the crucible.

This self-protection effect can be explained by a film formation on the inner walls of the graphite crucible. This film with its metallic aspect can be seen in Fig. 3b after the removal of the solidified ingot with 20 wt.% zirconium content. The phase analysis of this film revealed the presence of zirconium carbide ZrC in it. It is inter-

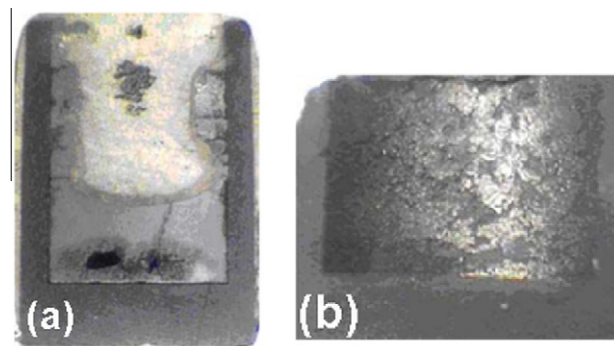


Fig. 3. (a) Longitudinal section of a crucible after the melting of water reactor corium with increased zirconium content. The crucible was not attacked by the corium melt. (b) The same crucible after the removal of the solidified ingot. A shining film was formed on the inner walls of the crucible.

esting to underline that the carbide phases were not found in the solidified melt. After this observation, the ZrC was considered to be a good candidate for the corium resistant coating. Compared to the NbC + TaC coating, the use of ZrC has the advantage of not bringing new elements in the chemical Zr–O–U–C system. The ZrC coating was thus chosen for experiments with prototypic water cooled reactor corium.

3.2. Fabrication of the ZrC-coating

3.2.1. Experimental procedure

The method of ZrC-coating application was developed in IAE NNC RK. It was shown that a successfully ZrC-coated crucible can be used for melting of oxide mixtures with no fear of crucible wall erosion and water reactor corium components carburization.

The coating application method, called reactive wetting, is based on heating until melting a zirconium layer which is disposed on the inner walls of the crucible. As a result of preliminary experiments it was revealed that the molten zirconium wets very well the graphite surface at temperature about 1900 °C. The molten zirconium is likely to react with the graphite surface and to form the zirconium carbide coating.

The used crucible was made of carbon graphite of R4340 reference. To make the zirconium layer, a split ring made of metal zirconium sheet was placed in the crucible (Fig. 4). This ring was 0.8 mm thick and its external diameter was equal to the internal diameter of the crucible.

It was wedged in the upper part of crucible and well stuck to crucible walls. The crucible with its zirconium sheet was then heated up to 1900 °C. The plateau at this temperature lasted 3 min.

3.2.2. Results and discussion

The obtained coating (Fig. 5) was about 50 μm thick at the upper part of the crucible, 70 μm thick in middle and lower part

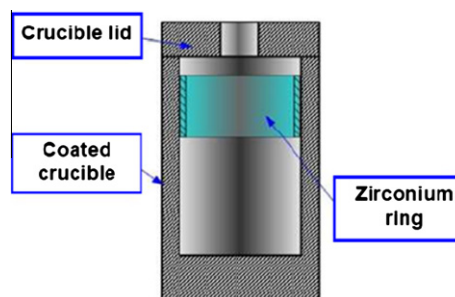


Fig. 4. Scheme of the crucible loading for ZrC-coating application.



Fig. 5. Longitudinal section of the graphite crucible with its ZrC-coating.

and 150 μm at the bottom of the crucible. The mass of zirconium necessary for complete coating of the crucible was about 0.15 g/cm². X-ray diffraction (XRD) analysis of the coating showed presence of sub-stoichiometric zirconium carbide.

The ratio between weight of loaded zirconium and the area of crucible internal surface allowing obtaining a uniform layer was estimated experimentally. This ratio depends on the type of the used graphite, the size of the crucible and the vertical gradient of temperature in the crucible during its heating. Two conditions revealed to be essential:

- It is necessary to provide a very good contact between the zirconium foil and the internal surface of the graphite crucible.
- It is necessary to provide the greatest possible rate of heating up to the melting temperature of zirconium to outstrip a premature zirconium carbidation.

The way the metal zirconium pours in the crucible can change in case of large size crucibles.

ZrC protective coating has been used in IAE NNC RK on graphite plasmatoms nozzles surfaces during performance of large-scale experiments with 60 kg of prototypic corium (U_x, Zr_y) O_{2-z} devoted to research of in-vessel retention (IVR) processes with imitation of decay heat in corium in the framework of ISTC project INVECOR.

4. Experimental studies of the ZrC-coating interaction with different corium melts

4.1. Resistance of the ZrC-coating to water cooled reactor corium

4.1.1. ZrC-coating interaction with (U_x, Zr_y) O_{2-z} corium

4.1.1.1. Experimental procedure. The efficiency of the obtained ZrC-coating was tested at high temperature with different prototypic water reactor corium loadings. The experiments were performed under argon atmosphere. The initial chamber pressure was 1.5×10^5 Pa. The final pressure was 1.8×10^5 Pa. Two experiments are reported here. The tested corium composition of the first test was 78 wt.% UO_2 + 22 wt.% ZrO_2 . The maximum reached temperature was 2650 °C. The plateau of the first experiment lasted only 5 min. The other reported experiment was made with 76 wt.% UO_2 + 9 wt.% ZrO_2 + 15 wt.% Zr composition. The maximum reached temperature was 2600 °C. It was performed with longer keeping at high temperature to estimate the resistance of the coating to high-temperature corium: the plateau lasted 40 min. At the

end of the both plateaus the generator was cut which led to a rapid cooling of the system.

4.1.1.2. Results and discussion. The crucibles after experiments are shown in Fig. 6. Neither erosion nor dissolution of the internal surface of graphite crucible was observed for the two crucibles. The ZrC-coating showed to resist enough to long-time keeping in high temperature corium.

The phase analysis of solidified melt samples showed, that the initial composition was transformed to the solid solution of a (U_x, Zr_y) O_2 type, where indexes X and Y depend on the ratio of initial components. The melts were not polluted with carbon coming from the coating or the crucible.

As a result of these experiments, we can conclude that ZrC-coating resists well to water reactor prototypic corium.

4.1.2. ZrC-coating interaction with (U_x, Zr_y) O_{2-z} -steel mixture

Stainless steel is the main structural material in nuclear reactors. It becomes thus necessary to study the corium melt with stainless steel inside. The amount of steel added in corium fits with the evaluated amount according to the reactor design and is equal to ~10% of corium mass.

4.1.2.1. Experimental procedure. The experiments with steel were performed in the VCG-135 test facility using the graphite crucible with previously applied ZrC coating. For simplicity of the results analysis, carbon steel was used instead of stainless steel. This allowed neglecting the corium-nickel and corium-chrome interactions. The loading was composed of 69.2 wt.% of UO_2 pellets chips, 8.5 wt.% of ZrO_2 fine powder, 13.2 wt.% of fragments of zirconium tube and 9.1 wt.% of steel rods. The maximum reached temperature was 2320 °C. When the temperature about 2300 °C was reached, a temperature reduction was registered and gas release from the melting volume was observed.

4.1.2.2. Results and discussion. The cut surface section of the crucible after the test is illustrated in Fig. 7. Contrary to loads without steel, an interaction took place between corium and the graphite crucible. The ZrC-coating was attacked by the corium which led to the carburization of the melt.

The sample diffractograms were obtained from sections surface containing mainly dark or light material. The main phase in the dark ingot material was solid solution ($\text{U}, \text{Zr}(\text{Fe}))\text{O}_{2-x}$. The main

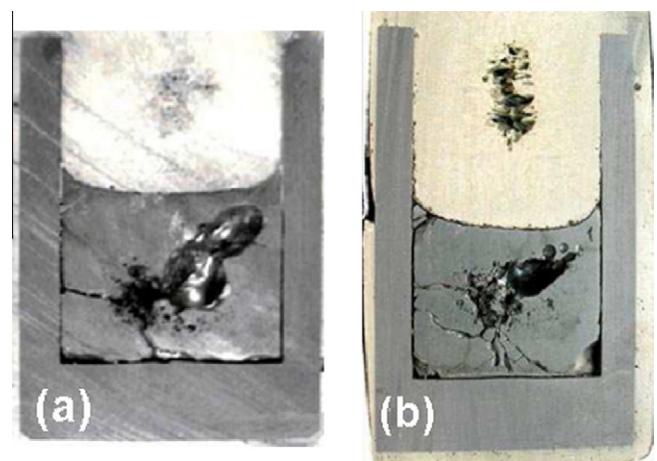


Fig. 6. (a) Longitudinal section of a ZrC-coated crucible after the heating of 78 wt.% UO_2 + 22 wt.% ZrO_2 mixture at 2650 °C during 5 min, (b) longitudinal section of a ZrC-coated crucible after the heating of 76 wt.% UO_2 + 9 wt.% ZrO_2 + 15 wt.% Zr mixture at 2600 °C during 40 min.



Fig. 7. Longitudinal section of a ZrC-coated crucible after the heating of 69.2 wt.% UO_2 + 8.5 wt.% ZrO_2 + 13.2 wt.% Zr + 9.1 wt.% steel mixture at 2320 °C.

phases in the light ingot material were carbide UFeC_2 and mixed oxide–carbide solid solution $(\text{Zr}, \text{U}, (\text{Fe}))(\text{C}, \text{O})$. As conclusion, two immiscible melts were formed in the ingot at high temperature, one “oxide” and one “carbide”. The undesirable carbide phase formed because of the attack of the ZrC-coating which led to the carburization of the melt.

It is not astonishing, that the presence of stainless steel components in corium melt degrades distinctly the protective characteristics of zirconium coating. The steel components are indeed known for their high chemical activity when they are overheated at the melting point of the oxide corium components.

It was seen previously that ZrC resists to UO_2 – ZrO_2 –Zr melt. The coating attack is thus due to the presence of steel in the melt.

Thermodynamic calculations in the Zr–C–Fe system were performed with GEMINI2 code [9] coupled to NUCLEA_08 thermodynamic database [10] to explain the reaction which took place between steel and ZrC-coating. The steel was here assimilated to iron to simplify the calculations. The quality criteria for the three binary systems included in the Zr–C–Fe system in the NUCLEA_08 database are considered as “Acceptable”. That means that these

systems are considered to be well known and satisfactorily modelled.

The interaction between 75 at.% Fe and 25 at.% ZrC (62 wt.% Fe and 38 wt.% ZrC) is illustrated on the graph in Fig. 8, where weight fractions of materials are plotted against the temperature. According to the graph, iron melts between 1450 °C and 1550 °C. Then ZrC dissolves progressively in the liquid iron. These results are in accordance with the phase diagram established by Shurin and Dmitrieva [13], where a eutectic point was determined at 1475 °C for 4.3 wt.% of ZrC. The system considered in our calculations is on the right side of this eutectic point. The liquidus of the system is thus higher than the eutectic temperature.

To limit the consequences of the ZrC–stainless steel interaction, a special device able to discharge the steel sample once the corium is liquid was developed in IAE NNC. With this device, which is represented in Fig. 9, it is possible to avoid a too long contact between the ZrC-coating and the overheated steel. It is made of a graphite tube (1) installed coaxially inside the crucible. The graphite tube is equipped with a sliding shutter (2) that is rod-connected (3) with electromagnet (4). It is controlled from the VCG-135 operator console.

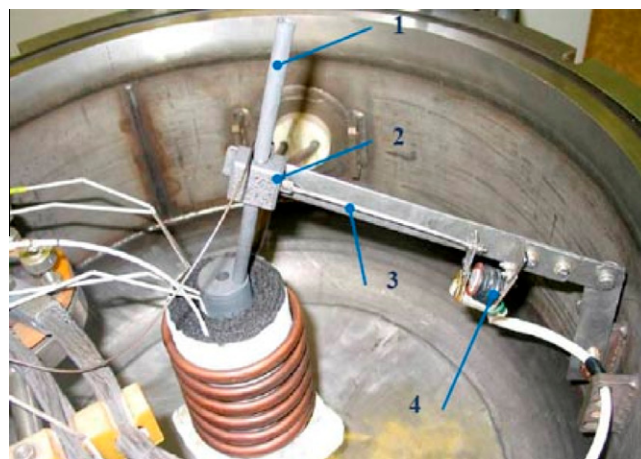


Fig. 9. Device for steel dropping into the VCG-135 crucible. (1) graphite tube, (2) sliding shutter, (3) rod connection, (4) electromagnet.

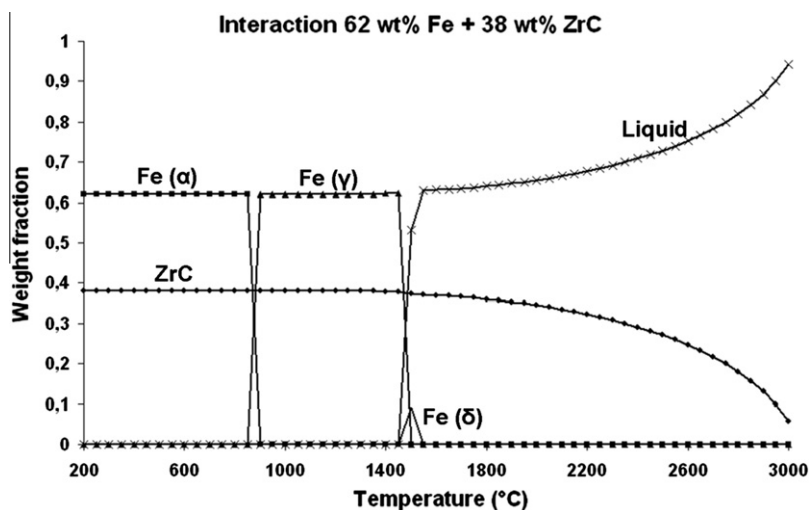


Fig. 8. GEMINI2 + NUCLEA_08 calculation simulating 62 wt.% Fe + 38 wt.% ZrC interaction. On the graph, weight fractions are plotted against the temperature.

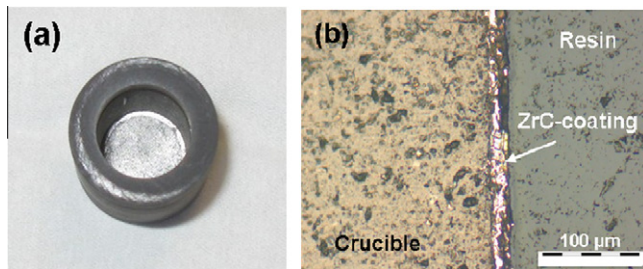


Fig. 10. (a) View of the ZrC-coating produced in the graphite crucible in VITI facility, (b) optical micrograph of the ZrC-coating produced on the interface of the graphite crucible.

4.2. Interaction of the ZrC-coating with sodium fast reactor corium

The experiments on the interaction between the ZrC coating and the prototypic sodium fast reactor (SFR) corium are performed in the PLINIUS experimental platform at CEA Cadarache, in the VITI facility [7,8,14].

The system UO_2 –stainless steel– B_4C is not well known to date, and even less its interaction with ZrC. Indeed, the whole system UO_2 –stainless steel– B_4C has never been studied. Because of this lack of data, the present experimental study was begun with the UO_2 – B_4C system. In this subsystem, only the phase diagrams U–B [15,16], B–U–C at maximum temperature of 1600 °C [17] and U–O–C at maximum temperature of 1700 °C [18] are known.

The study of the subsystem UO_2 –stainless steel and its interaction with ZrC can be assimilated to the study described in the previous paragraph concerning the water reactor corium.

The quantities of materials introduced in the crucibles were calculated with regard to the postulated melting of a fuel assembly with a “Fusible Shutdown Device” [19] which contains B_4C on its top. The B_4C is retained by a fusible material, such as aluminium, which should melt in case of an increase in temperature and release the absorber material at fuel level to absorb neutrons. Such melted assembly with Fusible Shutdown Device should contain about 73 wt.% of the fuel, 7 wt.% of B_4C and 20 wt.% of stainless steel.

Then, some experiments were performed in ZrC-coated crucibles to study the oxide mixtures UO_2 – Al_2O_3 and UO_2 – Eu_2O_3 . Al_2O_3 and Eu_2O_3 are not classically part of the sodium fast reactor corium but could be introduced in the reactor in order to prevent recriticality [20,21]. That is the reason why the resistance of the ZrC-coating to the both oxide mixtures is reported here.

4.2.1. ZrC-coating interaction with UO_2 – B_4C mixture

4.2.1.1. Experimental procedure. The ZrC-coating was produced in the VITI furnace. The inner walls of the graphite crucible were cov-

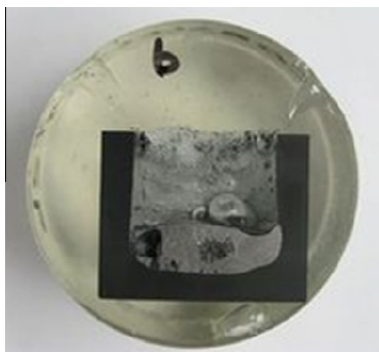


Fig. 11. Longitudinal section of a ZrC-coated crucible after the heating of 91.5 wt.% UO_2 + 8.5 wt.% mixture at 2200 °C.

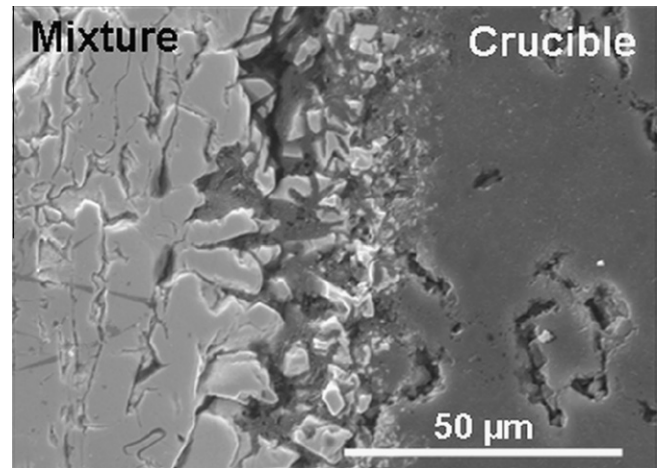


Fig. 12. Scanning electron micrograph of the interface between the crucible and the 91.5 wt.% UO_2 + 8.5 wt.% B_4C mixture.

ered by 25 µm thick film of 99.8% pure and annealed zirconium. Then the crucible was heated 100 °C over the melting temperature of the film (≈ 1850 °C). About 25 µm thick and uniform ZrC-coating was formed by diffusion of carbon to the zirconium liquid (Fig. 10a and b).

The studied mixture of UO_2 – B_4C contained 8.5 wt.% of B_4C and 91.5 wt.% of UO_2 . These proportions corresponded to those of the assembly with Fusible Shutdown Device, but without considering the stainless steel.

The UO_2 – B_4C mixture was prepared in a mortar and then introduced in a ZrC-coated crucible. The crucible heating was done until the melting of the mixture, i.e. 2200 °C (± 35 °C), during 90 min and the plateau last 30 min.

4.2.1.2. Results and discussion. One could notice in Fig. 11 that the ZrC-coating and the crucible were attacked. That means that the ZrC coating did not fulfil its function of protective barrier.

Further studies by scanning electron microscopy coupled with Energy Dispersive Spectrometry (SEM/EDS) clearly showed a chemical transformation of the coating.

At the lower part of the crucible, where the molten mixture was in contact with the coating for at least 30 min, the coating completely disappeared (Fig. 12). The same phase as in the middle of the ingot, containing B, C and U was detected at the interface between the mixture and the graphite crucible (Fig. 12). The chemical analysis revealed the absence of the zirconium element at the mixture–crucible interface.

The inside mixture melted around 2200 °C because of its carburization. Indeed, a heating test up to 2400 °C of the same mixture UO_2 – B_4C without carbon impurities in a tungsten crucible (without coating) did not lead to the melting [11,20]. That means that the interaction between the mixture and the ZrC-coating began in solid state.

To understand this interaction with ZrC, several studies of systems containing Zr, B and C were reviewed. The system Zr–B–C was investigated in details from 1400 °C to 3000 °C by Rudy and Windisch [22]. It was showed that B_4C and ZrC are never in equilibrium. An intermediate phase, ZrB_2 , which is very stable, systematically forms at solid state. Then, depending on the chemical composition, ZrB_2 can coexist with B_4C or with ZrC.

In other publications, the strong affinities of boron and carbon for the zirconium element were also observed. Indeed, the investigation of the B_4C –Zr interaction showed that a reaction between B_4C and Zr starts at 1250 °C and leads to the ZrB_2 and ZrC

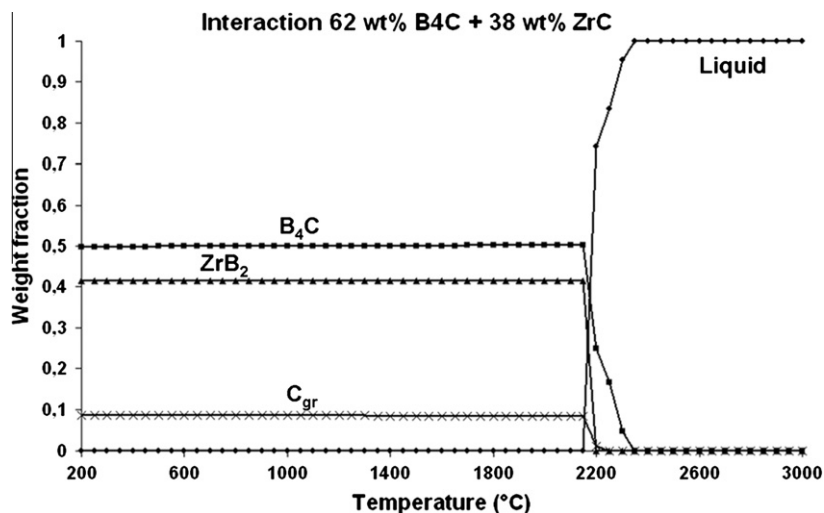


Fig. 13. GEMINI2 + NUCLEA_08 calculation simulating 62 wt.% B₄C + 38 wt.% ZrC interaction. On the graph, weight fractions are plotted against the temperature.

formation [23]. In the MASCA test program, interactions within the U–Zr–B–C–O system were studied [24]: ZrB₂ and Zr(C, O) were preferentially formed.

We showed previously that UO₂ does not react with ZrC. There are hence two possible explanations for the interaction leading to the ZrC disappearance: ZrC–B₄C interaction or ZrC–UB₄ interaction. According to GEMINI2 calculations, UB₄ is the boride phase which should have been formed in absence of carburization. [11].

Some thermodynamic calculations in the Zr–C–B–U system were performed with GEMINI2 code [9] coupled to NUCLEA (version 08) thermodynamic database [10] to understand the reaction which took place with the ZrC-coating. According to quality criteria for the binary and ternary sub-systems included in the U–Zr–B–C system, many information are missing in the Nuclea_08 database. In spite of that, the experimental study of the U–O–B–C system showed that GEMINI2 calculations are reliable enough [11].

These calculations were done with 25 at.% ZrC (arbitrary choice). In the graphs (Figs. 13 and 14), weight fractions of materials are plotted against the temperature.

The ZrC–B₄C interaction is illustrated in Fig. 13. With 25 at.% ZrC, which corresponds to 38 wt.% ZrC, ZrC interacts with B₄C to form ZrB₂. ZrB₂ is here in equilibrium with B₄C in excess. If ZrC

was initially in excess instead of B₄C, ZrB₂ would be in equilibrium with ZrC [22]. The melting of the whole system takes place here between 2150 and 2350 °C. These temperatures are in accordance with the melting temperature of the carburized UO₂–B₄C mixture. This explanation for the occurring interaction leading to the melt carbidation is thus possible.

The ZrC–UB₄ interaction is illustrated in Fig. 14. With 25 at.% ZrC, which corresponds to 11 wt.% ZrC, ZrC interacts with B₄C to

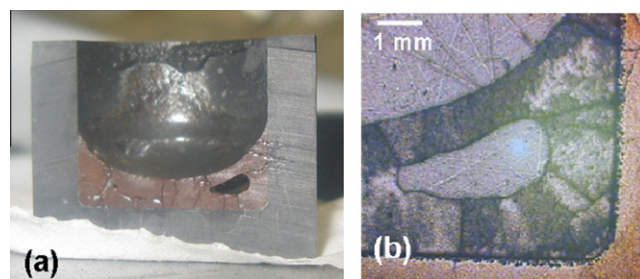


Fig. 15. (a) Longitudinal section of a ZrC-coated crucible after the heating of 48 wt.% UO₂ + 52 wt.% Al₂O₃ mixture at 1870 °C, (b) optical micrograph of this section.

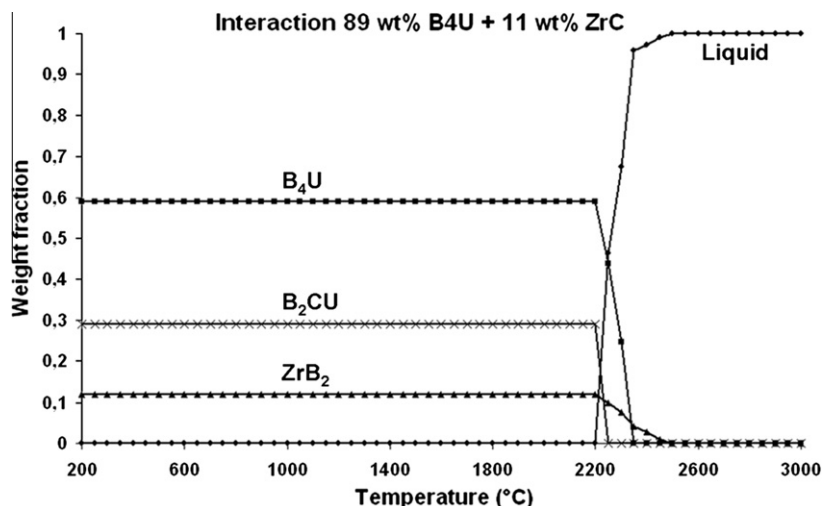


Fig. 14. GEMINI2 + NUCLEA_08 calculation simulating 89 wt.% B₄U + 11 wt.% ZrC interaction. On the graph, weight fractions are plotted against the temperature.

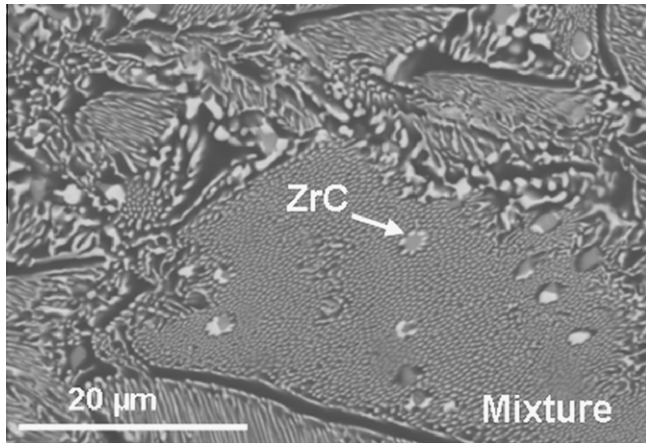


Fig. 16. Back-scattered scanning electron micrograph of the 48 wt.% UO_2 + 52 wt.% Al_2O_3 mixture contained in the ZrC-coated crucible, Black $\approx \text{Al}_2\text{O}_3$, White $\approx \text{UO}_2$, Grey $\approx \text{ZrC}$.

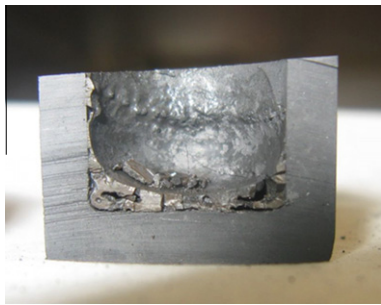


Fig. 17. Longitudinal section of a ZrC-coated crucible after the heating of 48 wt.% UO_2 + 52 wt.% Al_2O_3 mixture at 2000 °C. The coating was attacked and the load was carburized.

form ZrB_2 and UB_2C . Then, the whole system melts between 2200 and 2300 °C. These temperatures correspond also approximately to the experimental melting temperature of the carburized UO_2 – B_4C mixture. On the top of that, the transformation of the ZrC coating to ZrB_2 could make possible the diffusion of the carbon element to the mixture. This explanation for the occurring interaction is

thus also possible. Probably, the two interactions ZrC – B_4C and ZrC – UB_4 happen, depending on the local composition of the mixture near the coated crucible.

To conclude, the ZrC-coating is not adapted to experiments with loads which contain boron carbide B_4C . Contrary to experiments with steel where the ZrC-coating is dissolved by the melted steel, the mixture containing B_4C reacts with ZrC already in the solid state.

4.2.2. ZrC-coating interaction with UO_2 – Al_2O_3 mixture

4.2.2.1. Experimental procedure. Two experiments were performed with the UO_2 – Al_2O_3 mixture in the ZrC-coated graphite crucible: one with the quasi-eutectic 52 wt.% Al_2O_3 –48 wt.% UO_2 composition and one with the 40 wt.% Al_2O_3 –60 wt.% UO_2 composition [25].

Both powder mixtures were prepared in a mortar and then introduced to the crucible. The first mixture was heated until melting, i.e. 1870 °C (± 35 °C), and the second until 2000 °C (± 35 °C).

4.2.2.2. Results and discussion. As can be seen in Fig. 15, the crucible which was heated until 1870 °C was not attacked by the mixture UO_2 – Al_2O_3 . A further analysis of the interface between the mixture and the graphite crucible was done with a SEM coupled to EDS. It confirmed the non-carburization of the ingot.

As can be seen in Fig. 16, a little of ZrC was found to be dispersed in the middle of the mixture in the shape of small islands about 2 μm large. The ZrC stayed isolated independently to the other phases. There is also directly no carbon pollution directly in the melt.

The second crucible can be seen in Fig. 17. The ZrC coating did not resist to the UO_2 – Al_2O_3 mixture at 2000 °C.

GEMINI2 calculations were performed to understand the interaction between the studied mixture and the ZrC coating (Fig. 18). It was showed that the zirconium carbide starts to be consumed only at 2000 °C which is the temperature of this second experiment. Temperature is thus a determining factor to the resistance of the ZrC coating to the UO_2 – Al_2O_3 mixture. It can be also concluded that ZrC can be used as protective coating for graphite crucibles in case of oxide melt UO_2 – Al_2O_3 , only below 2000 °C.

4.2.3. ZrC-coating interaction with UO_2 – Eu_2O_3 mixture

4.2.3.1. Experimental procedure. The 75 wt.% UO_2 –25 wt.% Eu_2O_3 mixture was studied here [26]. The load was prepared in a mortar and heated in a ZrC-coated crucible up to 2100 °C (± 100 °C). A very

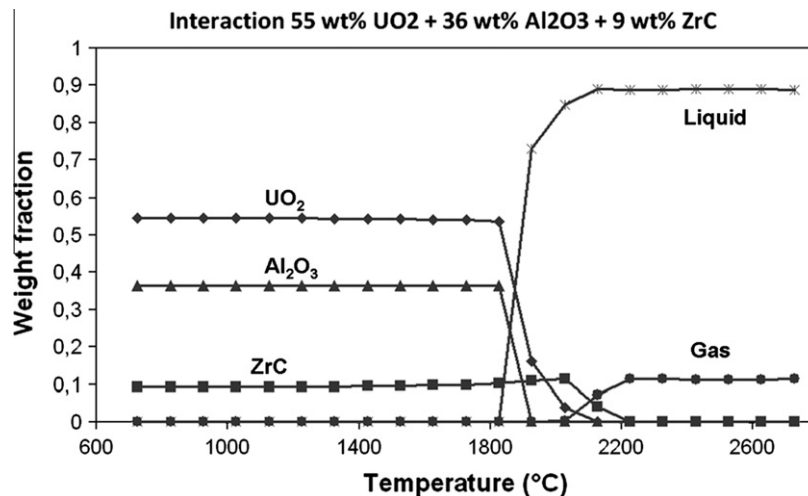


Fig. 18. GEMINI2 + NUCLEA_08 calculation simulating 55 wt.% UO_2 + 36 wt.% Al_2O_3 + 9 wt.% ZrC interaction, which corresponds to 60 wt.% UO_2 + 40 wt.% Al_2O_3 proportions. On the graph, weight fractions are plotted against the temperature.

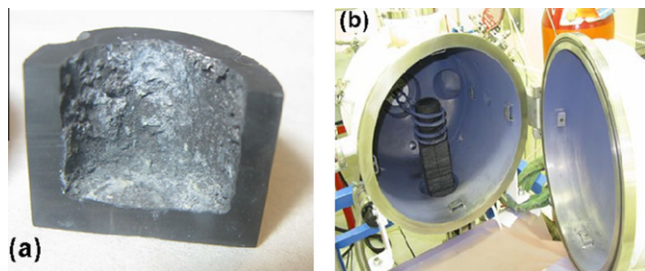


Fig. 19. (a) Longitudinal section of the ZrC-coated graphite crucible after the heating of the 75 wt.% Eu_2O_3 + 25 wt.% UO_2 mixture in it. The mixture did not melt but its carburization shows that the ZrC coating reacted with it. (b) Blue deposit $\text{Eu}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ on the VITI container walls, showing that the ZrC coating reacted with the Eu_2O_3 + UO_2 mixture. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

important gas emission took place from 1980 °C which made technically impossible exceeding 2100 °C.

4.2.3.2. Results and discussion. The UO_2 – Eu_2O_3 mixture did not melt in the crucible but sintered and slightly attacked the crucible. The empty crucible after the experiment can be seen in Fig. 19a. This point is confirmed by the XRD analysis of the inside products, which revealed that an uranium carbide UC had been formed. The gas emission was due to a reaction which took place between the mixture and the ZrC coating. Indeed, a thick blue coloured deposit, identified as $\text{Eu}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ by XRD, formed on the walls of the VITI chamber (Fig. 19b). The ZrC coating is thus not compatible with the UO_2 – Eu_2O_3 mixture. GEMINI2 calculations could not be performed within this chemical system because europium is not part of the NUCLEA_08 database.

5. Conclusion

Zirconium carbide has been selected as a refractory coating material which resists to Generation II and III Water Reactor oxidic corium melt ($\text{U}_x, \text{Zr}_y\text{O}_{2-z}$). It has been used as a protective coating on graphite crucibles to avoid the carburization of the studied corium melts. Reactive wetting of a melted zirconium foil on the graphite surface was chosen as technique of coating application. To ensure a homogenous coating, a specific process has been developed: especially a very good contact between the initial zirconium foil and inner walls of the graphite crucible must be provided. It is then necessary to apply the greatest rate of heating as possible up to the melting temperature of zirconium foil to avoid a premature zirconium carburization.

ZrC protective coating has been successfully used in IAE NNC RK on graphite plasmatrons nozzles surfaces during performance of large-scale experiments with 60 kg of prototypic corium ($\text{U}_x, \text{Zr}_y\text{O}_{2-z}$) devoted to research of in-vessel retention (IVR) processes with imitation of decay heat in corium in the framework of ISTC project INVECOR [27].

Besides the water reactor oxidic corium melt ($\text{U}_x, \text{Zr}_y\text{O}_{2-z}$), the coating was tested with the addition of steel. It was showed that overheated steel dissolves the ZrC-coating. To limit this undesirable phenomenon, a special device was developed in order to discharge the steel in the crucible only once the corium melted.

In the frame of studies for Generation IV sodium fast reactor safety, the mixtures UO_2 – B_4C , UO_2 – Al_2O_3 and UO_2 – Eu_2O_3 were considered. The coating revealed not to resist to the UO_2 – B_4C mixture because of the undesirable ZrC – B_4C and ZrC – B_4U reactions in solid state. The coating also does not resist to the UO_2 – Eu_2O_3 mixture: the $\text{Eu}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ compound is likely to form. Concerning the UO_2 – Al_2O_3 mixture, the ZrC-coating plays well its role of protective coating below 2000 °C.

Therefore the application range of this coating has been established: it is very efficient for Zr-containing melts in the absence of boron or steel and can also be used below 2000 °C for some oxidic melts like UO_2 – Al_2O_3 .

Acknowledgments

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