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Research

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SSM perspective

Background

Radiation safety is of particular concern during power plant maintenance. Radionuclides produced by the neutron bombardment in the core during operation may accumulate on system surfaces such as the filter system or piping and contribute to the radiation field. Some ions that are prone to neutron capture often become trapped in the deposits on the fuel cladding surfaces, also called CRUD. It is important to understand how radionuclides become incorporated and released from the CRUD in order to increase radiation safety. Density functional theory (DFT) calculations have been used to gain a better understanding of CRUD formation and transformation in BWR and PWR.

Results

- Utilizing Ag+ adsorption and incorporation in CRUD as tracer element, a comprehensive possible understanding of CRUD formation and transformation in BWR and PWR emerges, i.e., ions become adsorbed as hydroxides and subsequent condensation reactions define the resulting oxide grain growth directions in the CRUD and Ag+ tracing H+.
- The concentration of Ag+ in early CRUD reflects the degree of generic supersaturation of metal ions in vicinity of the boiling zone. At later stages, the ions become integrated in the growing CRUD. Transformations in the deposit render surface-to-volume ratios reduced in the CRUD interior, and, in as much as the Ag+ ions are aliovalent to both NiO/NiFe2O4 (PWR) and Fe2O3/Fe3O4/NiFe2O4 (BWR) CRUD:s, consequently, silver ions is understood to become enriched on the resulting interfaces.
- At the high concentration limit, delafossite was shown to offer a viable structural motif for intercalation of the aliovalent Ag+ in the oxides corresponding oxides, more so in the BWR ferrites than in PWR NiO. The latter is consistent with observations of looser CRUD in PWR and more profound in BWR, as determined by the different boiling conditions experienced by the corresponding fuel surfaces.
- The aliovalent Ag+ is in contrast to Co2+ that is readily incorporated as (Fe,Co)Fe2O4 and (Ni,Co)Fe2O4 in magnetite and nickel ferrite.
- Enrichment of radionuclides in metastable PWR CRUD is understood to become problematic during shutdowns where the CRUD becomes subject to disintegration and CRUD particles become adsorbed to piping surfaces outside of the core, rendering in worst case maintenance delayed. Less problematic is BWR CRUD owing to its chemical stability.
- The fate of intercalated AgFeO2 follows from literature, where transformation into metallic silver particles results. Formation of spurious silver particles in the CRUD, and these originating from Ag+(aq), would comprise smoking-gun evidence for the proposed understanding. Such experimental undertaking is encouraged.
- The incorporation of Ag+ in CRUD is contrasted by the Antimony deposition on the fuel cladding. In case of the latter, we find Sb(III) to readily adsorb, albeit reversibly, to the cladding oxide scale comprising ZrO2. Antimony incorporation in the scale requires further oxidation to Sb(V), e.g., owing to radiolysis of water in vicinity of the fuel. This suggests that maintaining the oxidizing conditions on power plant shutdown would mitigate Antimony dissolution into the coolant. Thereby, possible subsequent deposition on piping surfaces would be avoided.

Relevance

Knowledge of how radionuclides become incorporated and released from the CRUD is essential in order to increase radiation safety at nuclear power plants in the long term. SSM has contributed to the development of models that increase the understanding of CRUD formation and transformation in both BWR and PWR. Through funding a group of researchers at Chalmers University of Technology, SSM has also contributed to the maintenance of national competence within nuclear radiation safety.

Need for further research

This report provides a theoretical foundation for further development of models that could help decrease the deposition on system surfaces in a long term.

Project information

Contact person SSM: Elena Calota
Reference: SSM2021-6193 / 4530012

Atomistiska studier av radionukliders adsorption och desorption på bränslecrud och systemytor i lättvattenreaktorer

Sammanfattning

Denna studie handlar ytterst om arbetsmiljön för personalen vid planerade stopp för underhåll av reaktorerna. Reaktorns hjärta är härden där bränslet, som utgörs av rörbuntar bestående av zirkoniumlegeringar organiserade i speciella sammanhållande konfigurationer, där energin som frigörs vid kärnsönderfallen går till att värma en cirkulerande energibärare. I våra svenska kärnkraftverk är det vatten som är energibäraren. Vattnet som värms upp till nära 400 ^{o}C i härden är trycksatt. Annars skulle det koka bort. Det heta vattnet leds till värmeväxlare där värmeenergin överförs till ett icke-trycksatt cirkulerande vattensystem som driver en ångturbin. Det är där elektriciteten alstras. Det cirkulerande trycksatta kylvattnet är ett medium för transport och omfördelning av såväl oxidationsbetingelser som korrosionsprodukter.

I reaktorhärden utsätts kylvatten och korrosionsprodukter för strålning. Bestrålat vatten genomgår partiell radiolys, som åstadkommer en mer oxiderande miljö i reaktorhärdens närhet. Vattenkemi och filtersystem är designade för att hålla kylvattnets kemiska sammansättning stabilt. Som del av detta stationära tillstånd ingår utfällning och återupplösning av metalloxider på såväl bränslestavar, härd, rörsystem och värmeväxlare.

Övermättnader orsakade av lokal partiell kokning resulterar i en speciell form av utfällning på bränslestavarna, så kallad CRUD, en förkortning för ”Chalk River Unidentified Deposit”. (Trots att vår kunskap om dessa avlagringar är betydlig större idag än det var när begreppet myntades, så har vi ändå behållit det.) I kokvattenreaktorer (BWR) bildar dessa beläggningar stabila avlagringar. CRUD som bildas i tryckvattenreaktorer (PWR) är i hög grad instabil, så mycket så att den lätt löses upp vid nedstängning. Oavsett om det rör sig om en BWR eller en PWR så gäller att vid nedstängning blir kylvattnet mindre oxiderande.

Den kemiska sammansättningen hos korrosionsprodukterna som bygger CRUD är en spegel av alla de material som är i kontakt med kylvattnet. Där ingår även grundämnen som kan absorbera neutroner och vars atomkärnor därmed blir instabila gentemot sönderfall. Dessa radionuklider inbegriper Co-58, Co-60, Ag-110m, Sb-124, Sb-122, Cr-51, Mn-54, I-131, Cs-137. Sannolikheten för bildning av radionuklider ökar med uppehållstiden i härden. Därför sker en anrikning av dessa isotoper med tiden i och med CRUD-bildningen. Vid nedstängning frigörs dessa radionuklider delvis, mer i PWR än BWR, och fastnar på insidan av rörsystemen som ska servas. Denna källa till strålning fördröjer handhavandet och förlänger kraftverkens stopptid.

I två teoretiska studier har vi beskrivit hur kobolt, silver och antimon beter sig som resultat av hur de anrikas i olika värdoxider. I dessa studier använder vi oss av kvantmekanik för att beskriva de kemiska processerna, så kallad kvantkemi, där Schrödingerekvationen (SE) utgör grunden för vår kvantmekaniska förståelse. Även om SE är korrekt, så är den otymplig, ja nära nog omöjlig att lösa för annat än väldigt små molekyler. En genväg till de egenskaper hos lösningarna till SE, som är relevanta inom kvantkemin, efterfrågas därför. Den erbjuds lämpligt nog av täthetsfunktionalteori, DFT som står för ”Density Functional Theory”. Idag finns effektiva skräddarsydda beräkningsmetoder implementerade i behändiga datorprogram som möjliggör kvantkemiska beräkningar baserade på DFT. Dessa metoder har revolutionerat kemin och materialfysiken till den grad att experimentell forskning utan en DFT-baserad underbyggnad är nära nog otänkbar. De behändiga grafiska gränsytorna förenklar modelleringsarbetet och den snabba responsen från allt starkare datorer gör forskningen spännande. I vår forskning sätter vi upp hypoteser baserade på observationer och beskriver hur dessa är sammanlänkade via kemiska transformationer och mellansteg. Syftet med den resulterande ”mekanistiska förståelsen” är att hitta sätt att genom ändrade förutsättningar under reaktorlika förhållanden, styra de spontana kemiska vägvalen på ett sådant sätt att bildandet av oönskade svårhanterliga produkter undertrycks och önskade premieras.

Resultaten från beräkningarna visar stöd för att kobolt anrikas i oxider som bildar inversa spineller, t.ex. Fe_3O_4 och $NiFe_2O_4$. Genom tillsats av zink premieras istället bildning av en normal spinell $ZnFe_2O_4$, något som bibehåller Co^{2+} löst i kylvattnet, undviks att det fäster på rörytor och istället fångas upp i filtersystemet. Det senare eftersom tillsats av Zn^{2+} i överskott även undertrycker icke-specifik yt-adsorption av M^{2+} joner, inklusive Co^{2+} och Ni^{2+}, som utgör förutsättningen för bildning av de oönskade inversa spinellerna $(Ni,Co,Fe)Fe_2O_4$. Oxiderande förhållanden under nedstängning premierar även Fe_2O_3 hematit före Fe_3O_4 magnetit, vilket också blockerar koboltutfällning och bibehåller kobolten löst i kylvattnet.

Till skillnad från de två-värda jonerna Co^{2+}, Zn^{2+}, Ni^{2+}, så är silverjonen en-värd Ag^+. Källan till radionukliden av silver (Ag-110m) har sitt ursprung i packningsmaterial. En möjlig mekanism för anrikning och inkorporering av denna ”främmande” jon i de CRUD-bildande oxiderna, som främst består av NiO och $NiFe_2O_4$ men även Fe_3O4 och Fe_2O_3, påvisades genom Monte Carlo simulering respektive atomistiska elektronstruktur-beräkningar. I PWR bildas företrädelsevis NiO baserad CRUD. Motsvarande silverbärande struktur som påvisades med täthetsfunktionalteori utgjordes av ett delafossitmotiv, en lagerstruktur bestående av $Ag(I)Ni(III)O_2$ interkalerat i Ni(II)O som bildas samtidigt med att den senare växer i 111 riktningen. I BWR bildas CRUD bestående av $NiFe_2O_4$ men även Fe_3O4 och Fe_2O_3. Även i detta fall kunde den möjliga existensen av det delafossitbaserade motivet $Ag(I)Fe(III)O_2$ för inkorporering och anrikning av Ag^+ underbyggas medelst DFT på $Ag_4Fe_{27}O_{40}(s)$. Observationen att BWR-CRUD är mer stabil än PWR-CRUD visade sig även föra med sig att förmågan att binda in Ag^+ är större för BWR-CRUD än för PWR-CRUD. Den föreslagna mekanismen för anrikning av silver i metastabila delafossitmotiv - genom att yta/volym kvoten minskar allteftersom tiden går och CRUD avlagringen konsoliderar (s.k. Ostwald mognad) - kan förklara hur det är möjligt för små metalliska silverpartiklar (mindre är mikrometerstora) att bildas i CRUD.

Även källan till radionukliderna av antimon (Sb) har sitt ursprung i packningsmaterial. Antimon uppvisar två oxidationstal Sb(III) and Sb(V). Den oxiderande miljön i bränslets närhet motiverar att vi utgår från det högre oxidationstalet när vi försöker förstå hur Sb anrikas på zirkoniumbaserade bränsleinkapslingen som avslutas med ett naturligt växande oxidskikt bestående av monoklin zirkondioxid mon-Zr(IV)O_2. Det är naturligt att betrakta transformationen där kemiskt bunden Sb(III)@ZrO_2 oxideras av radiolyserat vatten till att bilda Sb(V)@ ZrO_2 i värdmatrisen. Den förra, Sb(III), tvingas till att vara en yt-specie p.g.a. dess steriska icke-bindande 5s5p-hybridiserade elektronpar. Den senare, Sb(V), tillför en nominell elektron till ledningsbandet i Zr(IV)O_2 värdstrukturen. Under oxiderande förhållanden går denna ledningselektron till att reducera en hydroxylradikal $OH^{\cdot}$ till hydroxidjoner OH^-, som i sin tur fås att neutralisera den rymdladdning som uppstått p.g.a. att en +V jon (Sb^{5+}) härbärgeras in en +IV (Zr^{4+}) position, d.v.s. Sb(V)@ Zr(IV)O_2. Omvänt, för att frisätta Sb(V) från ZrO_2 matrisen krävs reduktion till Sb(III) för att på så sätt få exponera denna för kylvattnet.

Sammanfattningsvis, så finner vi att kemin för Co^{2+}, Ag^+ och Sb(III)-Sb(V) uppvisar tre olika principer för inbindning till bränsleytan, två i samband med CRUD-bildning (Co, Ag) och en på ZrO_2 (Sb). För kobolt beskrevs inverkan av Zn^{2+} både för att frisätta Co^{2+} och för att undvika åter-deposition. För silver beskrevs hur Ag^+ inkorporeras som delafossit-analog i CRUD och underströks vikten av att hålla oxiden intakt genom att vidmakthålla oxiderande förhållanden under nedstängning. För antimon beskrevs hur ZrO_2 matrisen utgör den naturliga värdoxiden under oxiderande förhållanden. Följaktligen föregås Sb-frisättning av reduktion från +V till +III. Liksom fallet var för silver, undviks oönskad icke-specifik adsorption av $Sb(OH)_3$ på rörytor, genom att upprätthålla oxiderande förhållanden under nedstängningsfasen. Därmed undertrycks frisättningen från såväl CRUD som från näraliggande ZrO_2-täckta bränsleytor. Denna förståelse riktar sig främst till BWR. CRUD i BWR är ju är mer stabil än i PWR. I BWR gäller det således att behålla radionukliderna bundna i CRUD-avlagringen. I PWR är CRUD närmast att likna vid ett ludd som vandrar mellan bränslestavarna. För PWR stödjer därmed vår förståelse eventuella ansträngningar att utveckla tillsatser som stabiliserar detta CRUD-ludd på bränslet inför avstängning.

Content

1. Introduction

Robustness of structure and maintenance protocols for nuclear power plants stand on two complementary legs: Empirical knowledge of *how* pressure vessel, fuel, piping, heat exchanger load bearing materials behave under relevant conditions, and *why* they behave the way they do. The empirical studies produce data from laboratory testing under conditions that model those in the power plant. Physics based studies are performed to explain observations and to test possible interrelations between the empirical data.

The physics-based approach builds on presumed causality of events in explaining their evolution. Fundamentally, these events evolve owing to transformations on the atomic length scale, in the coolant, at interfaces and in the solid state. Reformulation of quantum mechanics by the density functional theory DFT has allowed chemically relevant properties of the Schrödinger equation to be extracted. This, in conjunction with ever larger computer power, more efficient algorithms and handy program packages, continue to facilitate the study of increasingly more relevant models of real processes from 1st principles. Multiscale modelling is resorted to for bridging between atomistic events and the macroscopic properties. Here, the periodic boundary conditions may be readily utilized to *seamlessly* connect the chemical and macroscopic length scales by means of DFT electronic structure calculations to arrive at viable reaction processes. Thus, a state-of-the-art scientific *modus operandi* for formulating rational working hypotheses is at hand, i.e., explaining old observations and predict new ones, and in doing so aiding in the formulation of new critical experiments.

Radiation safety is of particular concern during powerplant maintenance. Radionuclides that are produced by the neutron bombardment in the core during operation may accumulate on piping surfaces and contribute to the radiation field. Time in core is a decisive factor in radionuclide formation. It is enhanced if the ions that are prone to neutron capture become trapped in deposits on the fuel cladding surfaces. Such deposits form owing to local boiling, so-called Chalk River Unidentified Deposit (CRUD), is named after the place where they were first discovered [1]. Its sources include all metal surfaces in contact with the coolant, reflecting oxidation and subsequent oxide dissolution-reprecipitation processes involving mainly hematite, magnetite, nickel iron spinel and nickel oxide. In the reactor coolant, they appear in the forms of colloids/solid particles and soluble species. The local vaporization of water causes generic local supersaturation of solutes in the coolant and fuel CRUD deposition. Being dependent of coolant impurity and additive concentration levels, the phase compositions of fuel CRUD may vary. For example, in Swedish Boiling Water Reactors (BWR), fuel CRUD consists of hematite and nickel ferrite and it grows at a rate of ~1 μm/year [2-5]. In some BWRs with zinc injection, fuel CRUD may consist of zinc ferrite [5] and even zinc silicates. In Swedish Pressurized Water Reactors (PWR), on the other hand, NiO is a dominant phase. Historically, there have been incidents that excessive fuel CRUD was formed on fuel cladding surfaces, causing CRUD Induced Localized Corrosion (CILC) of fuel cladding materials in BWRs [6] and CRUD Induced Power Shift (CIPS) in PWRs [e.g. 7,8]. A coral reef analogue is in place when discussing the generic morphology of CRUD i.e., offering an open outer pore structure that is gradually lost inward owing to densification processes. Thus, the CRUD growth mechanism relies on the integrity of the pore structure that is understood to offer shelter to less robust and indeed fluffy transient structures resulting from the supersaturation conditions owing to the local boiling, transient precipitates that would else be carried away by the rapid and highly turbulent coolant flow. Such densification is ubiquitous in BWR while PWR remains fluffy to the extent that it dissolves on shutdown. A generic solidified core structure emphasizing coexistence of open and closed pores in conjunction with a Monte Carlo simulation of the fluffy regions is shown in Figure 1 and in Supporting Information 1.

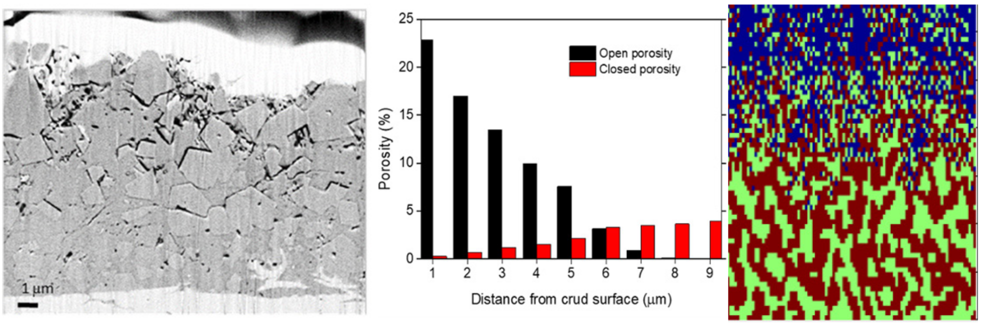

Figure 1: Electron microscopy image of a CRUD cross section (left), experimental porosity analysis (center) [9] and Monte Carlo simulated CRUD densification (right).

When uninterrupted, the boiling induced formation of CRUD is understood to offer a steady-state sink for all dissolved species in the coolant. In vicinity of the nuclear fuel where the neutron flux is high, some ions such as Cobalt(II), Silver(I) and Antimony(III-V) are particularly prone to transform into Co-58, Co-60, Ag-110m and Sb-124 radionuclides. In as much as the likelihood of this activation increases with the residence times in the CRUD, understanding of how radionuclides become incorporated and released from the CRUD becomes essential for efficient and safe powerplant management. The radionuclides formed during normal operation may become absorbed in the CRUD or released into the coolant. In case of the latter, they become trapped in the filter system or deposit on piping surfaces to cause radiation field elevation in general. There were indeed reported incidents that excessive radiation field owing to Ag-110m deposition, originating from control rod ware and seal rings [10,11] on PWR auxiliary systems that was built up during PWR shutdown operation [12-15], causing prolonged service downtime. Ag-110m is found to deposit on cold surfaces and while it is readily captured in the cation exchange resin under oxidizing conditions, it slips through under reducing conditions [15] causing the authors to reassess the reference [12]. Antimony is known to originate from graphite pump bearings and seals [11]. The Sb-124 radionuclide origin and release on shutdown is less extensively studied [16]. Here, it is proposed to form and adsorb to the zirconia scale on the fuel cladding prior to release on shutdown.

The purpose of our effort throughout is to provide fundamental principles on which best practice routines could be based. For LWRs such plant strategies to control out-of-core radiation field buildup may include (1) keep coolant impurity level low and the formed fuel CRUD stable so that little fuel CRUD dissolves during plant operation (BWR/PWR) and (2) keep fuel surfaces clean by ultrasonic cleaning of all fuel bundles before fuel reloading (PWR) or pre-film the piping surfaces with iron oxides after a plant decontamination campaign (BWR). The former may require that the coolant is properly conditioned (e.g., pH control in PWR and coolant iron to nickel ratio control in BWR).

The present work builds and extends on generic insight for BWR that has been developed concerning the interplay between Co-60 and (a) hematite Fe_2O_3 and magnetite Fe_3O_4, (b) inverse spinel in general and $NiFe_2O_4$ in particular, and (c) normal spinel of $ZnFe_2O_4$ [17]. Decisive for irreversible incorporation is speciation, i.e., cobalt partially substituting (1) Fe(II) in Fe_3O_4 while avoiding Fe(III) in Fe_2O_3, (2) Ni(II) in inverse spinel $NiFe_2O_4$, while (3) avoiding the Zn(II) site in the normal spinel $ZnFe_2O_4$. On supplying Zn(II) to the coolant, reprecipitation of the inverse spinel $NiFe_2O_4$ becomes suppressed by the competing formation of the normal spinel $ZnFe_2O_4$. In as much as Co(II) substitutes for Ni(II) in $NiFe_2O_4$ but not for Zn(II) in $ZnFe_2O_4$, addition of Zn(II) to the coolant maintains Co(II) dissolved in the coolant. Furthermore, specificity in absorption is contrasted by the non-specific Co(II) adsorption to hydroxylated surfaces and interfaces. In case of the latter, excess Zn(II) addition to the coolant causes the adsorbed Co(II) to desorb owing to ion-exchange processes. The two effects, suppression of Co(II) absorption during spinel reprecipitation processes, and the knock-out" effect acting on non-specific Co(II) adsorption to the spinel interfaces, were taken to explain observed Co-60 absorption prevention as well as the rapid release of Co-60 upon additions of Zn(II) to the coolant prior to shut down. This was arrived at in [17] by probing the free energy landscapes for non-specific adsorption and ion exchange, as well as for Co(II) adsorption leading absorption, cf. Figure 2.

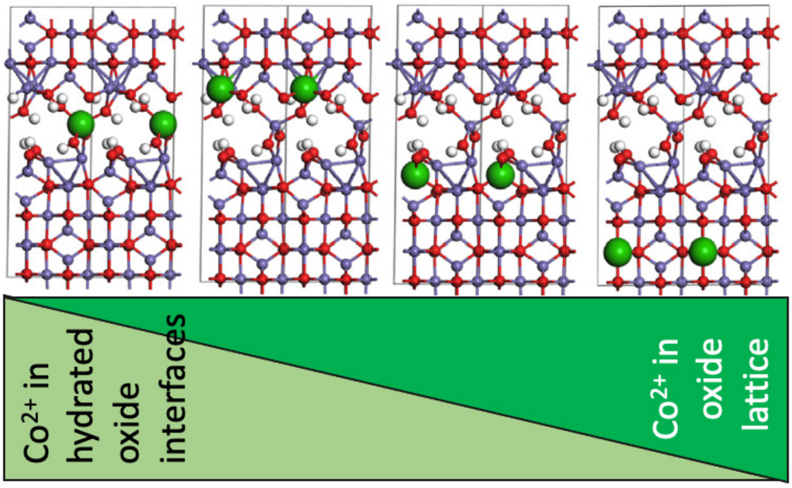

Figure 2: Schematic reaction path connecting Co^{2+} adsorption to corresponding absorption in $NiFe_2O_4$

Robustness of our findings by means of density functional theory (DFT) calculations is warranted because both grain boundary and interface models are treated as heterostructures in the solid state. Indeed, it is paramount, when exploring reactions energy landscapes by means of DFT, that the fundamental bindings in reactants and products are of similar character, i.e., so-called isodesmic reactions[1]. This way, well known inherent flaws of DFT can be made to cancel. Thus, the internal energies of the composite describing the complex interfaces (nominal reaction products) are compared to the internal energies of relevant elementary reference components (nominal reactants). Here, the latter comprise the relevant elementary metal oxides, metal hydroxides, and water. Once the assessment is made of the relative robustness of an interface structure - being fundamentally inaccessible by means of experiment but made available by means of 1st principles DFT - the further connection to experimental energetics is made via the known Gibbs energies of formation of the said reference compounds.

In the present study, we generalize our modelling strategy, developed for Co-60, to include Ag-110m in CRUD. Throughout, radionuclides are understood to come in trace concentrations and co-precipitation to render the compounds formed by the majority

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[1] An isodesmic reaction is a chemical reaction in which the type of chemical bonds broken in the reactant are the same as the type of bonds formed in the reaction product. This type of reaction is often used as a hypothetical reaction in thermochemistry.

elements discriminating templates. Preliminary results and considerations regarding radionuclides of antimony are provided in Appendix.

2. Ag^+ in PWR CRUD

PWR CRUD consists mainly of NiO. It is understood to form by consecutive deposition resulting in nominal $Ni(OH)_2(s)$ deposits that undergo condensation reactions

$$2\,Ni(OH)_2(s) \rightarrow Ni_2O(OH)_2(s) + H_2O(g)$$
$$Ni_2O(OH)_2(s) + Ni(OH)_2(s) \rightarrow Ni_3O_2(OH)_2(s) + H_2O(g)$$
$$\ldots$$

In general, we obtain

$$Ni_{n-1}O_{n-2}(OH)_2(s) + Ni(OH)_2(s) \rightarrow Ni_nO_{n-1}(OH)_2(s) + H_2O(g)$$

DFT is resorted to in order to compute how the stability of the hydroxylated interface depends on NiO lamella thickness. Rapid convergence with systematic increasing thickness of NiO lamella is found, see Figure 3.

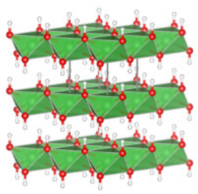
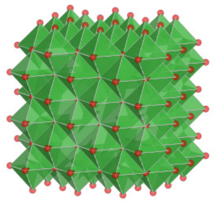
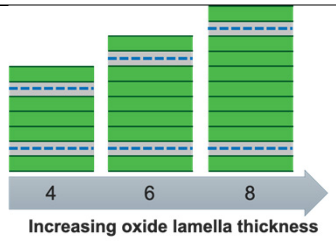
Bulk references		$n\,NiO+Ni(OH)_2 \Rightarrow Ni_nO_{n-1}(OH)_2$, for n=4-8	Lamella thickness	ΔH (kJ/mol)
$Ni(OH)_2$ 	NiO 		4	-32.09
			6	-31.72
			8	-29.69
(a)		(b)	(c)	

Figure 3. (a) Periodic crystal structures (bulk) of Nickel(II) hydroxide ($Ni(OH)_2$) and Nickel(II) oxide (NiO). (b) Lamella thickness stabilization reaction of $Ni(OH)_2$ incorporated in NiO and schematic representation of lamella growth (n represents the number of NiO units between a $Ni(OH)_2$ layer). (c) Enthalpy of formation (ΔH) for the lamella stabilization for thickness of n=4-8.

The model for PWR CRUD is built based on NiO lamellas that grow preferentially in [111] direction of the NiO crystal. It is known that the NiO (111) surface is unstable due to the lack of lateral charge screening. The surface will be termination by either O^{2-} or Ni^{2+} ions, i.e., NiO(111) is a polar surface [18]. However, the oxygen-terminated NiO(111) surface is readily hydroxylated when in contact with water molecules that provide hydroxyl groups (OH^-) [19]. Hydroxyl groups stabilize the polar (111) surface by partial compensation of the lateral charge screening. Furthermore, condensation of $Ni(OH)_2$ causes the stacking of NiO lamella and thus grain growth. Hence, as PWR CRUD is found in an aqueous environment, the hydroxylated NiO(111) surface model is suitable for the study of the growth and ion incorporation in CRUD. It is noted in Figure 3 how layered $Ni(OH)_2$ upon condensation converts into NiO while growing along the [111] direction of the latter.

Our current understanding of possible silver sources in the reactor coolant and how Ag species are formed in LWR fuel CRUD is limited. Since Ag-110m is considered to always be present in reactor coolant and in fuel CRUD, one suspects that it may come from the corrosion release of Ag-containing seals that are in contact with reactor coolant. In case of an excessively high amount of Ag in the reactor coolant, the source may even be seal debris accidently released during service. In the present study, however, we focus on the scenario of interplay between $Ag^+(aq)$ in the coolant and NiO(s) as fuel CRUD, trying to understand how $Ag^+(aq)$ may get incorporated in NiO.

In as much as the said hydroxylated interfaces provide sites for non-specific binding of Ag^+, i.e., by replacing H^+, possible incorporation in NiO in CRUD precipitates is addressed. One possible limiting case would comprise an intercalated a delafossite motif, i.e. of $Cu(I)Fe(III)O_2$-type. Here intercalation by $Ag(I)Ni(III)O_2$ in NiO is considered, see Figure 4.

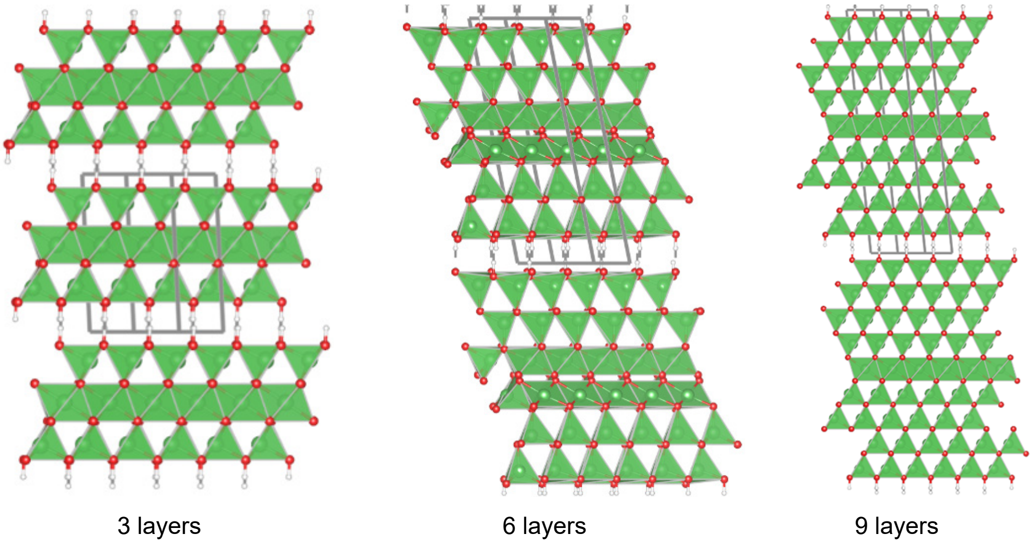


Figure 4. Ag+ intercalation in oxygen terminated 111 planes of NiO, 3, 6, 9 NiO layers.

DFT was resorted to for assessing the stability of this compounds toward decomposition into $AgNiO_2$ and NiO, while confirming also the analogy between Ag^+ and H^+ by considering in addition $HNiO_2$, i.e. NiOOH, see Figure 5.

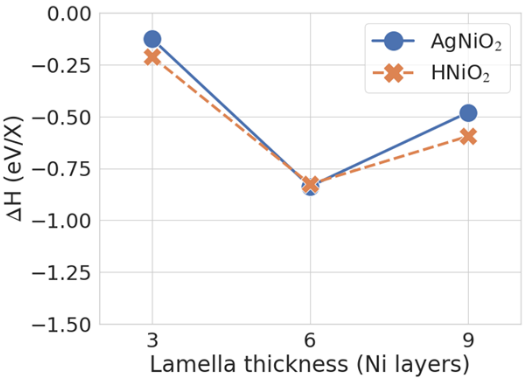


Figure 5. Resulting energetics for decomposition of the structures in fig.4 towards formation of $AgNiO_2$(s) and NiO(s).

Note that while stability of this compound toward disproportionation was demonstrated, it is understood to be exotic in that it mixes Ni(II) and Ni(III). In as much as PWR conditions have low P_{O2}, $Ag(I)Ni(III)O_2$ is not expected to be stable. Upon intercalation however, this species is understood to become stabilized owing to partial delocalization of the nominal hole associated with the Ni(III) moiety in the NiO matrix. Still, a NiO based CRUD that incorporates $AgNiO_2$ is expected to be metastable, in agreement with observation.

3. Ag^+ speciation in BWR

We acknowledge the fact that under BWR conditions CRUD is mainly composed Fe_2O_3, Fe_3O_4 and its structural analog $NiFe_2O_4$. We envisage it to form owing to the water chemistry, where local boiling produces local supersaturation of Fe^{2+} that precipitates as ferrous hydroxide $Fe(OH)_2$ and Goethite FeOOH that transform by dehydration into magnetite and hematite respectively, according to

$$2\ FeOOH(s) + Fe(OH)_2(s) \rightarrow Fe_3O_4(s) + 2H_2O(g)$$
$$2\ FeOOH(s) \rightarrow Fe_2O_3(s) + H_2O(g)$$

Kinship between the magnetite Fe_3O_4, i.e., $Fe(II)Fe_2O_4$ and nickel ferrite $Ni(II)Fe_2O_4$ inverse spinel emerges from the corresponding reaction with the corresponding hydroxides

$$2\ FeOOH(s) + Fe(OH)_2(s) \rightarrow Fe(II)Fe_2O_4(s) + 2\ H_2O(g)$$
$$2\ FeOOH(s) + Ni(OH)_2(s) \rightarrow Ni(II)Fe_2O_4(s) + 2\ H_2O(g)$$

Throughout this study, the inverse spinels were modelled by magnetite as the central conclusions are understood to carry over to the nickel iron spinel prevalent in the BWR CRUD.

Moreover, in as much as the main assumption in the present study, common to both BWR and PWR is $Ag^+(aq)$ substituting for H^+ at non-specific hydroxylated interfaces of the growing CRUD, see Figure 6.

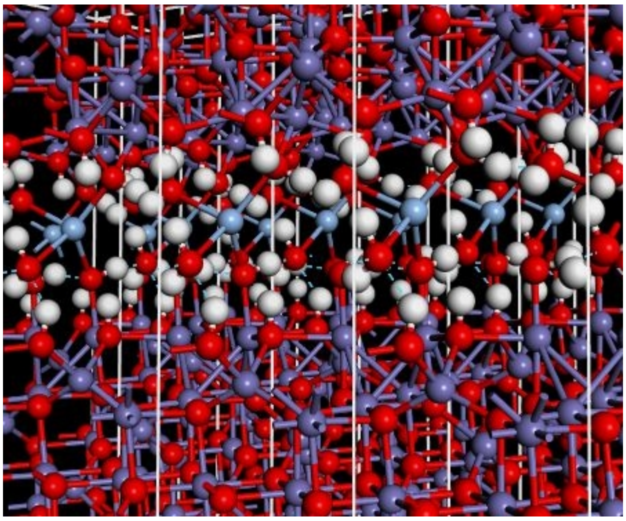


Figure 6. Generic representation of hydroxylated transition metal oxide interface including exchanges of H^+ by Ag^+.

It follows that also the delafossite type speciation may carry over from $AgNiO_2$@NiO to the iron oxide-based CRUD that forms in BWR. And this so much so that indeed the delafossite mineral comprises $Cu(I)Fe(III)O_2$, where Ag(I) is understood to replace Cu(I) [20], see Figure 7.

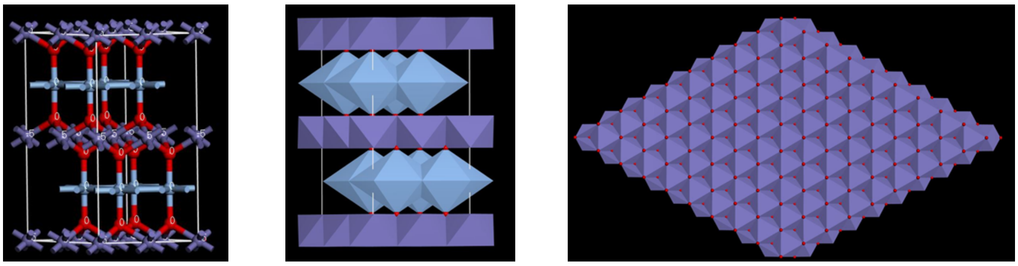


Figure 7. Delafossite $AgFeO_2$. Left:. Ball and stick representation. Center: Structural building blocks. Right: FeO_2 layer composed of octahedral coordinated Fe(III) ions.

The viability of this option was tested. Because the CRUD is ill-defined, we employ two reference systems to assess the stability of possible intercalated Ag(I) ions. These matrix compounds comprise αFe_2O_3 and γFe_2O_3 being magnetite and maghemite, respectively. First, contact is made to experiment by computing

$$Ag_2O(s) + \alpha Fe_2O_3(s) \rightarrow 2AgFeO_2(s) \qquad \Delta H = -36 \text{ kJ/mol}$$
$$Ag_2O(s) + \gamma Fe_2O_3(s) \rightarrow 2AgFeO_2(s) \qquad \Delta H = -56 \text{ kJ/mol}$$

The analogous reaction may be assessed after allowing magnetite to coarsen. Two cases were considered, one directly associated with the magnetite structure in that while the oxygen terminated (111) plane is fully occupied in the oxygen sublattice, yet, it has vacancies in octahedral sites. The second option comprises displacement of adjacent Fe(III) ions initially residing in tetrahedral sites into said octahedral sites thereby completing the oxygen terminated (111) planes compatible with delafossite see Figure 8.

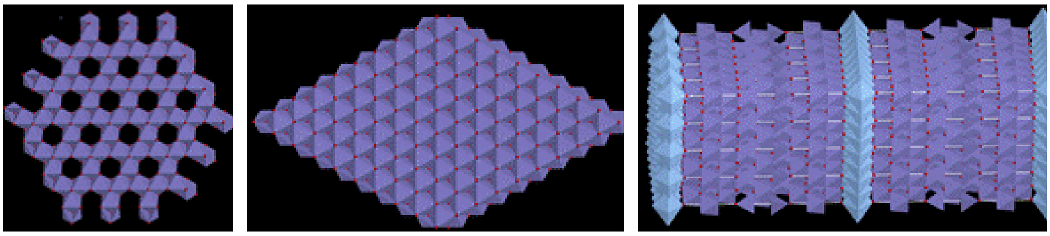


Figure 8. Left: Oxygen terminated $Fe_{1-x}O_2$ (111) plane with vacant octahedral sites in Fe_3O_4. Center: Resulting FeO_2 plane in Fe_3O_4 upon displacement of adjacent Fe(III) ions initially residing in tetrahedral sites into vacant octahedral sites. Right: Resulting intercalation of $AgFeO_2$ structural element in magnetite.

To assess the viability of theses and analogous structures forming, we consider the reactions

$$2Ag_2O(s) + 6Fe_2O_3(s) + 5\, Fe_3O_4(s) \rightarrow Ag_4Fe_{27}O_{40}(s)$$
$$\Delta H = +\, 133 \text{ kJ/mol (outer } Fe_{1\text{-}x}O_2 \text{ – magnetite reference)}$$
$$\Delta H = +\, 13 \text{ kJ/mol (outer } Fe_{1\text{-}x}O_2 \text{ – maghemite reference)}$$
$$\Delta H = -\, 82 \text{ kJ/mol (relaxed defect free } FeO_2 \text{ interface)}$$
$$\Delta H = -\, 202 \text{ kJ/mol (relaxed defect free } FeO_2 \text{ interface – maghemite reference)}$$

Having confirmed that the delafossite motif is indeed robust relative to Ag_2O and Fe_2O_3 reference reactants, the stability of the system was tested further by considering the reaction that employs the $AgFeO_2$ in conjunction with a combination of hematite/maghemite and magnetite as reactants. We obtain for

$4AgFeO_2(s) + 4Fe_2O_3(s) + 5Fe_3O_4(s) \rightarrow Ag_4Fe_{27}O_{40}(s)$

$\Delta H = + 205$ kJ/mol (defective outer $Fe_{1-x}O_2$ – magnetite interface)

$\Delta H = + 125$ kJ/mol (defective outer $Fe_{1-x}O_2$ – maghemite reference)

$\Delta H = - 10$ kJ/mol (relaxed defect free FeO_2 interface)

$\Delta H = - 90$ kJ/mol (relaxed defect free FeO_2 interface – maghemite reference)

It is emphasized here that the most stable $Ag_4Fe_{27}O_4$ structure is indeed that possessing said relaxed defect free FeO_2 interfaces that accept the linearly coordinated Ag of delafossite. The fact that the $AgFeO_2$ incorporation in iron oxide associated CRUD is highly exothermic is in contrast to the more subtle intercalation of $AgNiO_2$ in NiO. The relevance of this observation is emphasized further by the fact that hard CRUD grows readily on BWR fuel, while PWR CRUD is thin and easy to remove.

4. Generic modelling by Monte-Carlo simulations

The chemical atomistic perspective had CRUD formation as being associated with accumulation of transition metal hydroxides that transform into corresponding oxide by condensing on the cladding surface owing to local boiling. Complementary Monte-Carlo simulation of CRUD formation and evolution was resorted to. This, to explore fundamental principles for CRUD initiation and evolution. The model utilizes random walk of particles on a grid that take place on different time scales. Modelling of CRUD initiation concerns adsorption of CRUD particles onto surfaces. Subsequent densification of CRUD towards surface is understood to result due to local vaporization and boiling. The long-time scale concern slow transformation whereby the dense CRUD undergoes crystallization to minimize surface-to-bulk ratio and thus reduce the concentration of undercoordinated surface sites, see Figure 9.

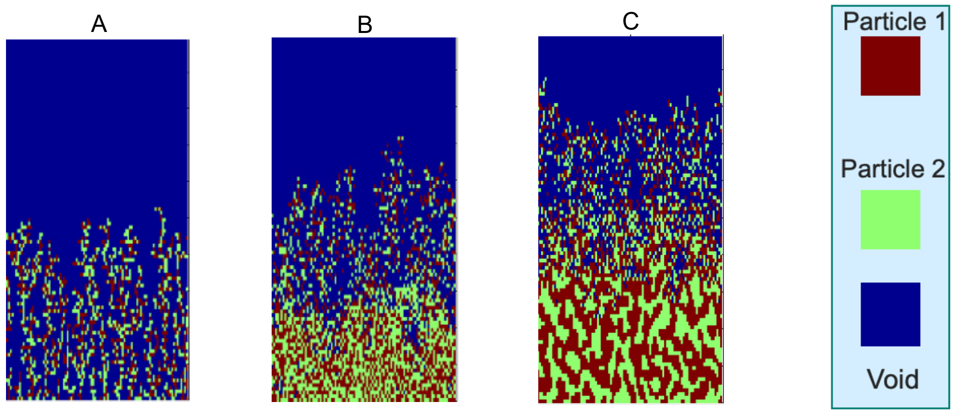


Figure 9. Model of CRUD growth from Monte Carlo simulations.
A. CRUD initiation: Form due to local boiling induced supersaturation
B. CRUD Densification: Vaporization induced implosion of structure
C. CRUD Transformation: Crystal growth by preference for neighbours of same kind.

5. Summary and conclusions

- Utilizing Ag^+ adsorption and incorporation in CRUD as tracer element, a comprehensive possible understanding of CRUD formation and transformation in BWR and PWR emerges, i.e., ions become adsorb as hydroxides and subsequent condensation reactions define the resulting oxide grain growth directions in the CRUD and Ag^+ tracing H^+.
- The concentration of Ag^+ in early CRUD reflects the degree of generic supersaturation of metal ions in vicinity of the boiling zone. At later stages, the ions become integrated in the growing CRUD. Transformations in the deposit render surface-to-volume ratios reduced in the CRUD interior, and, in as much as the Ag^+ ions are aliovalent to both $NiO/NiFe_2O_4$ (PWR) and $Fe_2O_3/Fe_3O_4/NiFe_2O_4$ (BWR) CRUD:s, consequently, silver ions are understood to become enriched on the resulting interfaces.
- At the high concentration limit, delafossite was shown to offer a viable structural motif for intercalation of the aliovalent Ag^+ in the oxides corresponding oxides, more so in the BWR ferrites than in PWR NiO. The latter is consistent with observations of looser CRUD in PWR and more profound in BWR, as determined by the different boiling conditions experienced by the corresponding fuel surfaces.
- The aliovalent Ag^+ is in contrast to Co^{2+} that is readily incorporated as $(Fe,Co)Fe_2O_4$ and $(Ni,Co)Fe_2O_4$ in magnetite and nickel ferrite.
- Enrichment of radionuclides in metastable PWR CRUD is understood to become problematic during shutdowns where the CRUD becomes subject to disintegration and CRUD particles become adsorbed to piping surfaces outside of the core, rendering in worst case maintenance delayed. Less problematic is BWR CRUD owing to its chemical stability.
- The fate of intercalated $AgFeO_2$ follows from literature, where transformation into metallic silver particles results [21]. Formation of spurious silver particles in the CRUD, and these originating from $Ag^+(aq)$, would comprise smoking-gun evidence for the proposed understanding. Such experimental undertaking is encouraged.
- The incorporation of Ag^+ in CRUD is contrasted by the Antimony deposition on the fuel cladding. In case of the latter, we find Sb(III) to readily adsorb, albeit reversibly, to the cladding oxide scale comprising ZrO_2. Antimony incorporation in the scale requires further oxidation to Sb(V), e.g., owing to radiolysis of water in vicinity of the fuel. This suggests that maintaining the oxidizing conditions on powerplant shutdown would mitigate Antimony dissolution into the coolant. Thereby, possible subsequent deposition on piping surfaces would be avoided.

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Appendix: On antimony in CRUD

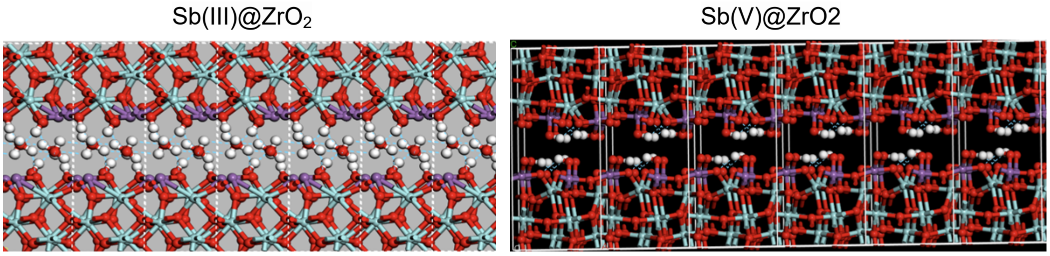
Enhanced probability of radionuclides to form by absorbing neutrons results from increased residence time in the core. Our studies have contrasted the speciation of Co(II) to that of Ag(I) in transition metal oxides, mainly iron oxides (BWR), nickel ferrites (BWR &PWR) and nickel oxide (PWR) .

Sb originates from graphite pump seals and bearings or from Sn in Zircalloy. Upon reactor shut-down Antimony (Sb) radionuclides are observed in the coolant and on piping surfaces [1].

Association of antimony to the CRUD, while owing to local boiling, is different. Given that ZrO_2 is readily accessible as it comprises a several mm thick passive film covering the entire fuel cladding, it is understood to offer support for the Sb(III) deposition. Preliminary realizations of chemical incorporation of antimony at $Zr(IV)O_2$ interfaces and subjected to structural optimization by means of DFT are shown in Figure S3.1. Both Sb(III) and Sb(V) were considered and found to be viable. The latter employs water as oxidant owing to radiolysis.

For reference, a standard procedure for doping of ZrO_2 involves co-precipitation of $ZrCl_4$ with $Sb(III)Cl_3$ to form $Zr(Sb)O_2$[2].

In conclusion: Sb(III)(aq) dissolved in coolant is suggested to deposit on ZrO_2 owing to local boiling. Subsequently, Sb(III)(ads) becomes oxidized into Sb(V) due to the radiolysis of water in the core. On shut-down, the pO_2 is reduced as radiolysis stops. Thus, Sb(V) becomes dissolved as Sb(III)(aq) that subsequently adsorbs to piping surfaces and increasingly so on cooling.


$Sb(III)@ZrO_2$

Sb(V)@ZrO2

Figure A1 Viable chemisorption of Sb(III) (left), and speciation of Sb(V) (right) on ZrO_2 passive film owing to local boiling induced supersaturation of coolant and subsequent oxidation by water subject to radiolysis.

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Supplementary information

Monte-Carlo simulation of CRUD formation and growth

The stochastic simulations are performed by defining a N_1xN_2 grid, where one side describes the cladding surface, from the opposite side particles are incoming with a defined flux or probability P_{flux}, and on the two adjacent sides periodic boundary conditions are defined.

There are four types of processes occurring simultaneously:

1. The supersaturated system in vicinity of the boiling surface is associated with particles (e.g. molecular clusters). It is modelled by incoming particles, defined as type 1 or 2, that move towards the surface as well as having a probability to move away perpendicular to the cladding surface, P_{perp}. Particles which reach the cladding surface stick to the surface with a probability $P_{stick,cladding}=1$.
2. Particles which come in contact with the already adsorbed particles that form the early CRUD, stick to them with a probability $P_{stick,CRUD}$.
3. The early CRUD is allowed to densify where larger CRUD parts may move towards the cladding surface due to external pressure corresponding to voids in the early CRUD imploding with a probability $P_{dens,CRUD}$ owing to local loss of solvent caused by the local boiling.
4. Aggregates growth and Ostwald ripening emerge spontaneously by allowing different particle types exchange place with probability, P_{sep} in order to maximize the number of neighbors of the same type.

DFT – Computational details

Spin-polarized calculations were performed based on DFT[1,2] in the implementation with plane-waves[3] and pseudopotentials using the CASTEP code [4]. The Perdew, Burke, and Ernzerhof (PBE) GGA functional[5,6] was employed in all calculations. Core electrons were described by on-the-fly generated ultrasoft pseudopotentials[7], and a plane-wave energy cutoff was set to 600 eV. The k-point sampling of the Brillouin zone was made by means of the Monkhorst-Pack scheme [8,9] with a 4x4x4 k-point mesh for all bulk structures and a 4x4x1 k-point mesh for all interfaces. The electronic structure was minimized until the total energy difference was smaller than 10^{-7} eV/atom for two consecutive SCF cycles. To facilitate convergency, a Gaussian smearing scheme with a width of 0.2 eV was used. All structures were fully optimized using the L-BFGS[10,11] algorithm with the total energy convergence tolerance of $2x10^{-5}$ eV/atom, maximum force tolerance of $5x10^{-2}$ eV/Å, maximum stress tolerance of 0.1 GPa, and maximum displacement tolerance of 10^{-3} Å.

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