ZIRCONIA-RARE EARTH OXIDE PHASE STABILITY PROGRAM IN SUPPORT OF ACR-1000® FUEL DESIGN

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ABSTRACT

The ACR-1000®[1] CANFLEX®[2]-ACR fuel bundle design is an evolution of the 43-element CANDU®[3] 6 CANFLEX Mk-4 fuel bundle. The central element of the bundle contains burnable neutron absorbers (BNA) (Gd, Dy) in a stabilized (Y) zirconia matrix with no fissile material.

This neutron absorbing material is not part of the traditional CANDU® experience. One activity identified in fuel design verification is the phase stability of the cubic solid solution that results during sintering as part of pellet manufacture of this material. This paper provides an overview of AECL's program to investigate the phase stability of this new material in support of the design verification effort in this area.

INTRODUCTION

The ACR-1000 is an evolutionary, Gen III+**[4], 1200 MWe class pressure tube reactor, designed to meet industry and public expectations for safe, reliable, environmentally friendly, low-cost nuclear power generation. The ACR-1000 retains basic CANDU design features such as: modular, horizontal fuel channel core, low-temperature heavy water moderator, water-filled vault, two diverse shutdown systems, on-power fuelling and an accessible reactor building for on-power maintenance. The improvements

[1] ACR-1000® (Advanced CANDU Reactor®) is a registered trademark of Atomic Energy of Canada Limited (AECL).
[2] CANFLEX® is a registered trademark of AECL and the Korea Atomic Energy Research Institute (KAERI)
[3] CANDU® (CANada Deuterium Uranium) is a registered trademark of Atomic Energy of Canada Limited (AECL).
[4] Gen III+ is the classification given to nuclear technologies by an international team, including Canada, that is collaborating on research to develop the next generation Gen IV reactors. The ACR-1000 is one of the technologies that is considered a generation III+ design.

implemented in the ACR-1000 are particularly evident in the core and fuel design. While retaining heavy water in the calandria for moderation, the coolant has been converted to light water. This reduces the required heavy water inventory by approximately 60%, reducing capital and purity maintenance costs.

The ACR fuel design is similar to the 43-element CANDU® 6 CANFLEX Mk-4 fuel bundle. It consists of 42 elements that contain low-enriched uranium (LEU) and central element that contains Burnable Neutron Absorber (BNA) pellets. The BNA pellets contain burnable poison (gadolinium and dysprosium), which increase safety margins by controlling the core reactivity during accident conditions. Building on the extensive use of oxides in the fabrication of fuel pellets, the BNA pellets were designed as a sintered mix of gadolinium, dysprosium, yttrium and zirconium oxides.

Phase stability describes effects on the crystallographic structure of the BNA material during reactor operation that has the potential to compromise the integrity of the fuel element. Changes in density and the volume induced by phase transformation are the primary concern. Verifying phase stability is the process of assessing whether these changes in BNA properties during operation are of design concern either in triggering sheath failure or in maintaining geometrical stability after sheath failure.

DESIGN VERIFICATION PROGRAM

Design verification is the process of determining and documenting that the design conforms to specified requirements. During this process, design features are verified to meet design requirements. It is a thoroughly planned and documented process subject to various Quality Assurance Standards that are captured in company-wide and project specific AECL procedures. Adherence to these procedures ensures that the design meets all customer and regulatory design and quality requirements.

The design requirement that drives the need for the phase stability program is the functional safety requirement: “Fuel bundle elements in the reactor shall contain the uranium fuel and its fission products in normal operation, anticipated operational occurrences (AOOs) and design basis accidents (DBAs), except for large break loss of coolant accident (LOCA) prior to emergency core cooling system (ECCS) establishment, the affected channel in single channel events, and inadvertent entrainment of small size debris in heat transport system (HTS) coolant.” This requirement is applicable to the central element; hence the need to understand the phase stability of the material used in this element.

In order to support the planned design verification, information regarding the phase stability of the BNA fuel element material is required so that an assessment can be made of centre element integrity. This information is also relevant to confirming manufacturability of the BNA pellets. The plan for the required research and assessment of this material was reviewed broadly in AECL to ensure sufficiency in addressing potential phase stability concerns. The program to examine phase stability of the BNA fuel element includes irradiations. These irradiations will take place in conditions close to ACR-1000 operating conditions. Preparatory theoretical and experimental works in this area are necessary to ensure that phase stability is preserved under laboratory conditions (no radiation fields) at representative temperatures.

Collaboration between AECL and the Royal Military College (RMC) has resulted in a unique opportunity to better address these preparatory activities. The Nuclear Fuel Group of the Chemistry and Chemical Engineering Department of the RMC is internationally recognized in the areas of fuel performance and thermodynamics , both aspects of this study. AECL has extensive experience and knowledge in design of nuclear components and irradiation experimentation. The experience, experimental and theoretical tools of these two organizations have exceptional depth to address possible concerns related to BNA phase stability.

PREVIOUS KNOWLEDGE

The phase stability program’s scope is determined based on an assessment of existing knowledge in regards to zirconium oxide behaviour. A brief summary of this knowledge assessment is presented here.

A considerable amount of information on zirconium oxide is available in the open literature. Zirconium oxides have been used in far ranging applications from diamond substitutes to medical uses. These oxides are commonly present in all CANDU reactors due to the oxidation of zirconium alloy components. Due to the extensive use of these alloys, a large number of oxidation and phase identification experiments have been performed in Canada and internationally.

Zirconium oxide was proposed and irradiated as an inert fuel matrix dating back to at least 1962. [1] It was and is considered as a potential inert fuel matrix for much the same reasons that it is incorporated in the ACR-1000 fuel as the BNA matrix: 1) It has a low neutron cross section 2) It accommodates actinide and lanthanide oxides resulting in stable compounds noted for irradiation stability. The ACR selected burnable poisons, dysprosium and gadolinium, are members of the lanthanide series.

There are three well-defined phases for pure stoichiometric zirconium oxide in order of increasing temperature: monoclinic ($T \lesssim 1000°C$), tetragonal ($1000°C \lesssim T \lesssim 2300°C$, and cubic ($T \gtrsim 2300°C$). The cubic phase is isomorphous with the cubic UO_2 structure. This cubic phase is also commonly referred to as the fluorite structure, which is a cubic anion sublattice in a cation face-centred cubic crystal structure that has the same arrangement as the fluorite mineral.

The monoclinic phase has the lowest density and the cubic has a more efficient packing structure and therefore the highest density. There is approximately a 6% density difference between the monoclinic and cubic arrangements. The tetragonal phase is very close in density to the cubic phase.
[2] Transformations between these oxide phases due to temperature changes (during fabrication and/or operation) are of concern because the associated density changes may threaten sheath integrity.

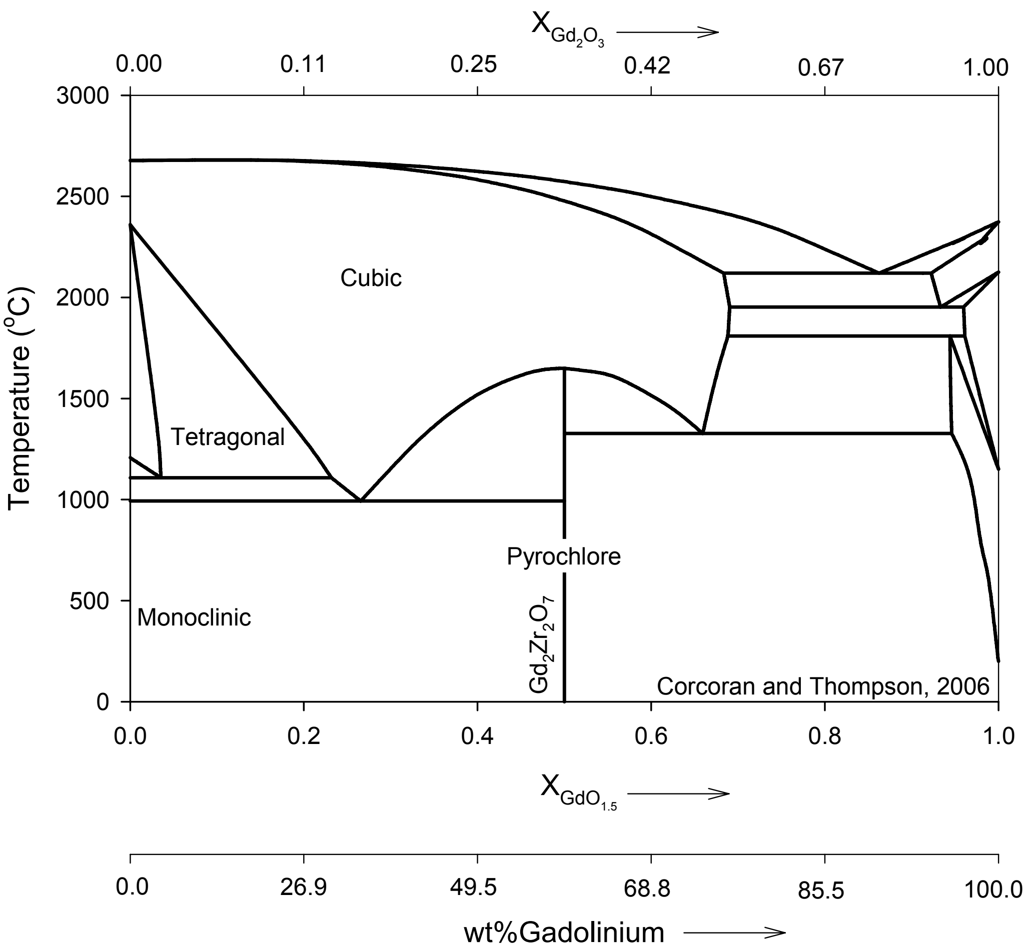

Figure 1: ZrO_2-Gd_2O_3 Binary Phase Diagram

Figure 1 presents a typical binary phase diagrams involving zirconium oxide and the BNA oxides. Notice the presence of the cubic region extending from 0-70mol% BNA oxide for temperatures higher than ≈1000 °C. In contrast the lower temperature phases are primarily two-phase regions. The composition of a two-phase region varies with temperature and composition. Since phase proportion influences density, this introduces an additional complication in the density control of the product during manufacture (sintering process).

From a neutronic behaviour perspective, a certain amount of BNA must be present within strict tolerances to achieve the desired safety margin. The amount of zirconium oxide (inert matrix) can be adapted to meet geometric requirements while maintaining the BNA content. Consequently, selection of a phase with wide margin in temperature and composition is desirable to accommodate possible variation in the manufacturing process. The extensive cubic single-phase region ensures this requirement.

It is widely reported that stress may induce phase transformation between monoclinic and tetragonal zirconium oxides. This behaviour makes it difficult to ensure the geometrical stability of a pellet under reactor conditions. Furthermore, the tetragonal structure is also known to degrade in humid atmospheres at temperatures around 200-300°C resulting in micro-cracking and phase transformation.[4] Conversely, cubic zirconium oxide has been shown to exhibit phase stability at reactor temperature and pH conditions. [5] [[6] This is a definite advantage of the cubic phase in preventing further deterioration of fuel elements with BNA pellets in case of sheath failure..

In order to stabilize the cubic zirconia phase, specific dopants are added to the zirconium oxide, which considerably lower the temperatures at which the cubic transformation occurs. The most common of these dopants are rare earth oxides (e.g., Y, Gd, Dy) of which yttrium oxide is the most common. The binary diagrams of zirconium oxide with dysprosium or gadolinium oxide show similar behaviour.

Open literature papers that have examined the irradiation stability of stabilized zirconium oxide have concluded it is between “good” and “outstanding.” [7] [8] [9][10] In contrast, the potential degradation of partially stabilized zirconium oxides is widely reported.[10]

Most irradiation applications have addressed the potential for zirconium oxide as an inert fuel matrix for use with actinides (e.g. uranium). Fission of actinides is a more energetic process than the neutron capture of BNA neutron absorbers. It has been proposed that the damage effects caused by fission fragments are the primary mechanism in the degradation of partially stabilized zirconium oxides under irradiation. If this is the primary mechanism, there is a strong possibility that even partially stabilized zirconia would not undergo phase transformation for the BNA application.[10]

A recent paper underscores the general irradiation tolerance and stability of the cubic fluorite structure and examined zirconium oxide derivatives explicitly. [11] The irradiation induced mechanism addressed in this paper is the amorphization of the oxide phase. The authors claim that the key to radiation tolerance is an inherent ability to accommodate atomic lattice disorder. They further suggest one step in determining irradiation stability is the study of the binary temperature-composition phase diagrams. They argue that chemical mixtures that exhibit ordered (line compounds) should be avoided and that mixtures that exhibit inherently disordered phases with wide ranges of stoichiometry (such as the cubic phase) should be more resilient to irradiation damage. These types of phases can accommodate radiation-induced defects because the reaction pair energy to induce the defect is small and so is the corresponding distortion of the lattice. They examined the relative resistance of a number of zirconium and lanthanide oxide compounds and concluded that a ZrO_2-Dy_2O_3 mixture is the one of the most resistant compounds to radiation-induced amorphization in the assessed oxide series. One conclusion is that greater stability of stoichiometric compounds at elevated temperature (such as the pyrochlore phase) lowers radiation tolerance. Although focussed on amorphization, the authors argue that the mechanisms they propose increase radiation damage effects in general.

In summary, based on the existing knowledge, the BNA material selected is a cubic fully stabilized zirconia matrix containing dysprosium, gadolinium, and yttrium oxides. This selection is supported by the thermal and irradiation stability reported by several authors from experiments on similar specimens.

Although well supported by the existing literature, it was considered prudent to confirm the stability of the selected compound as part of the design verification.

PHASE STABILITY PROGRAM

The purpose of the research performed under the phase stability program is to provide information to allow an assessment of the stability of the BNA compound under ACR-1000 operating conditions. There are three main activities to support the design verification. These activities are: binary and multi-component phase diagram generation, long-term annealing tests, and irradiation experiments. The binary and multi-component phase diagram generation was performed using F*A*C*T software (Facility for the Analysis of Chemical Thermodynamics). These diagrams are consistent with available information for similar systems based on experimental results and extend the phase boundaries. The information generated in this activity was used to confirm that the conditions used during the sintering process should produce a reproducible fully stabilized cubic structure.

Long-term annealing tests are being completed as part of the second activity. These tests were performed with temperatures covering the range that the BNA material will be exposed to during operations. These tests are expected to show that the BNA material is stable under operating temperatures. In this activity, samples are annealed at relevant temperatures over many months and periodically examined by X-ray diffraction for signs of phase change. This will address the possible concern that the high-temperature cubic phase may transform to low-temperature phases during long-term exposure to operating temperatures. This effect is considered very unlikely due to the relatively low temperature of BNA pellets during operation. Preliminary results from these tests suggest that temperature effects will not significantly affect phase stability, although no final conclusion will be drawn until the tests are completed.

The final activity is the in-reactor irradiation and PIE work, which are planned as final confirmation of BNA pellet stability. Irradiation will be conducted at temperatures and fluences as close to ACR-1000 conditions as possible. Phase verification using X-ray diffraction before and after irradiation will identify changes that may occur during irradiation. Pellet and element dimensioning will also be performed which will quantify integral effects.

SUMMARY

The assessment of phase stability of the BNA compound is part of the overall design verification of the ACR-1000 fuel design. There are three main activities to support this objective:

- Binary and multi-component phase diagram. Research using thermodynamic modelling has been completed to fully describe the BNA system. This knowledge is a valuable tool in assessing this and future design compositions for their potential application as BNA material. Furthermore, the open literature review provides support to the conclusions obtained in this activity and provide confidence of the BNA stability during irradiation
- Long-term annealing tests. These tests are near completion and the preliminary results suggest that temperature effects will not significantly affect phase stability
- In-reactor tests are in the advanced state of planning and components are being fabricated

The collaboration between industry and universities, in this case RMC and AECL, have proven to be a valuable tool in addressing technical challenges in nuclear fuel design.

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