Improving heat transfer in spent nuclear fuel disposal packages using metallic void fillers

by

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Master of Science in Nuclear Science and Engineering

ABSTRACT

Disposal packages containing high heat generating spent nuclear fuels (SNF) require improved heat transfer to keep the peak cladding temperature from going above the tolerance limit. Filling the accessible void spaces between the container and the SNF with a high heat conducting metal is a potential solution. In metal casting, it is well known that a gap forms at the metal-mold interface due to solidification shrinkage and it significantly reduces heat transfer during cooling. This negative heat transfer effect is persistent for a disposal package since the filler stays in the container after solidification. The key to close the gap is to promote metallic bonding by minimizing the oxidation of the container during the required preheating stage of the void filling process. However, direct contact between the container and the molten filler can lead to the growth of intermetallic phases, which can embrittle the container.

The contribution of this work is twofold. First, through a down-scaled experiment, it was shown that coating a steel container with Zn and using Zn or Zn-4wt.%Al as a filler and unidirectionally cooling the melt from the bottom successfully suppressed the formation of the gap. Closing the gap increased the effective thermal conductivity of the package by a factor of roughly 6 under the employed experimental conditions. Second, tests showed that using near eutectic Zn-Al and executing the filling process at a temperature below the melting point of Zn suppressed the growth of any intermetallic phases. Specifically, this prevents the growth of Fe-Zn intermetallic phases due to the sufficiently high composition of Al, and it inhibits the dissolution and diffusion of Fe from the container by extending the presence of the ZnO diffusion barrier, which delays the growth of the Fe-Al intermetallic phases.

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The credit also goes to the staffs at MIT CMSE, MIT Hobbyshop, and MIT PSFC machine shop for teaching me technical skills that were required for the study.

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CHAPTER 1. INTRODUCTION

1.1. Objective

Disposal packages containing high heat generating spent nuclear fuels (SNF) require improved heat transfer to keep the peak cladding temperature from going above the tolerance limit. Filling the accessible void spaces between the container and the SNF with high heat conducting metals and alloys can be a potential solution. This was tested earlier by a group of researchers in the 1980s where they used aluminum, lead, zinc, and their binary alloys [1]. However, their purpose of using it was for package stabilization and radiation shielding during transportation rather than improving heat transfer. Thus, the focus of their studies was on material compatibility such as liquid metal corrosion tests of light water reactor fuel assembly materials in molten metal, and further studies narrowed the best candidate down to lead [2]. Consequently, multi-directional cooling was preferred to uni-directional cooling to reduce the time of liquid and solid metal contact, and solidification shrinkage induced defects were not considered [3].

Amongst the solidification shrinkage induced defects, the so called air gap formation, which is the detachment of the solidifying metal from the mold, is known to significantly reduce heat transfer through the metal-mold interface [4]. Unlike metal casting, where only the casting is the final product, the solidified void filler stays in the container and, as a result, the negative heat transfer effect of the gap is persistent. This hinders fully utilizing the thermal benefits of using a metallic filler. The formation process of the air gap is well understood [4][5]. Initially, poured molten metal is partially in contact with the mold where the portion of the contact area depends on the surface
roughness of the mold. The boundary solidifies first and it detaches from the mold as the interior solidifies and shrinks. Thus, the formation of the gap can be suppressed by promoting metallic bonding between the casting and the mold. However, this is difficult since preheating the container is essential to prevent early solidification during the filling process and oxidation rate dramatically increases with increasing temperature. Especially for iron and carbon steels, the potential materials for the container [6], the length scale of the oxide layer thickness is in micrometers even after several seconds of exposure in air at high temperature [7]. Imperfections of the iron oxide layer or long term contact between the oxide and liquid metal occasionally allows liquid metal to penetrate through the oxide, forming intermetallic phases [8]. But such partial bonding is not strong enough to overcome the shrinking force [9]. Considering the dimensions of a SNF package, running the process under an inert environment can be complex and expensive. Using metal oxide reducing chemical agents can be inappropriate since they decompose and lose their functionality during the preheating step and leave salt residues even if the preheating temperature is below the decomposition threshold.

Kinetics of oxidation and the structure of the oxides depends on the base material. This means that the oxidation rate can be controlled while using the same container material by coating it prior to the filling process. Oxidation of zinc is well understood due to its application to semiconductors and the growth rate of zinc oxide is known to be slow [10][11], especially compared to iron and carbon steels. Besides, high thermal conductivity and an acceptably low melting point of zinc makes it a suitable material for this application. This study shows the feasibility of using a zinc coated container with zinc void filler to close the container-filler interfacial gap through a down scaled laboratory experiment. In addition to zinc, the widely used near eutectic zinc aluminum alloy, Zn-4wt.%Al, is also tested as a void filler and its benefits are discussed in detail.

1.2. Background bibliography

The application of the method developed in this study is aimed at disposal packages containing SNF from fast spectrum reactors, such as the conceptual SNF from Traveling Wave Reactors (TWR) [12], which is expected to have a much higher radioactive decay heat and higher peak-to-average power profile than the conventional Light Water Reactor (LWR) SNF. The focus is also on the deep borehole disposal (DBD) concept where only a small number of SNF is contained per package. The approximated radioactive decay heat of a TWR SNF is plotted in Figure 1 with that of a typical
pressurized water reactor (PWR) SNF for comparison. The decay heat equations used for each plot are also shown in the figure. The equation for the TWR SNF is from TerraPower and that of PWR SNF is from [13]. For information on the progress of the DBD method, see the reports from Sandia National Laboratories [14]–[17] and theses from the previous students in the MIT borehole group [18]–[26].

Designers have considered different kinds of materials as a SNF package void filler. The main purpose of these efforts was to stabilize the package during transportation, storage, and emplacement. A summary of such work can be found in a report from the Pacific Northwest National Laboratory [27]. A review article that discusses the requirements of void filler materials is also available [28].

**Figure 1.** Decay heat profile of a TWR SNF compared to that of a conventional PWR SNF. The equations that were used for the plots are included in the figure.
1.3. Importance of the work

Figure 2 shows an illustration of the DBD concept. We have the host rock at the outermost region, then the liner that stabilizes the hole, the gap, and then the waste package. The waste package consists of the container, the void filler, and the fuel assembly. As denoted in the figure, the package can be engineered prior to drilling and emplacement. Let us call this “pre-engineering”. On the other hand, the liner will be inserted into the hole during or after the drilling process and the gap will be filled with a low permeability material after emplacing the packages. Let us call these steps “post-engineering”. In addition to the two, we have the host rock, the natural environment of which humans can hardly engineer.

There are limits on controlling the post-engineering process. For example, from the heat resistance point of view, contact resistance will exist at every interface, i.e., between the host rock and the liner, between the filled gap and the liner, and between the package and the filled gap. However, the pre-engineering process can be fully controlled. This means we can design the package, apply any necessary technologies, inspect for any flaws, and therefore, assure its quality. In other words, we can minimize the contact resistance between the container and the void filler and the void filler and the fuel assembly.

**Figure 2.** An illustration of the borehole disposal concept with annotation on the pre-engineering and the post-engineering process and the natural environment. The dimensions are not to scale.
The parametric heat transfer calculation in Appendix C shows us the maximum temperature in the package plotted against the thermal conductivity (TC) of the void filler. One can question the necessity of having a high TC void filler because we can keep the temperature to below 200 °C even with an arbitrary void filler that has a TC close to unity. However, this calculation assumed a continuous media, neglecting all the contact resistance and any kinds of imperfection in the gap fill material and the host rock, e.g., porosity, fracture, or any incompletely filled region, which are aspects that we cannot fully control. Therefore, the basis mindset should be – it is hard to control the post-engineering process and the natural environment so let us maximize the benefits that we can achieve in the pre-engineering process. This is the aim of this study and it focuses on maximizing the thermal benefit of using a metallic void filler.

1.4. Thesis overview

Despite its eventual simplicity, the interfacial gap closure method introduced in the subsequent chapters emerged after much literature review, metallographic analytical thought, and several trials. The main section of the thesis, from Chapter 2 through Chapter 4, includes the essentials of the work. Chapter 2 explains the experimental setup in a concise manner but detailed enough so that readers can reproduce the results. Chapter 3 includes the results and discussion based on a question and answer style. The storyline goes from explaining the limitations of using pure Zn to emphasizing the benefits of using eutectic (or near eutectic) Zn-Al alloys based on the experimental results from this study and relevant literature. Chapter 4 summarizes the work with concluding remarks and suggests things to consider in a full-scaled experiment or in a practical application.

The setup and results from additional tests that can be useful to the reader are included in the Appendices. Specifically, Appendix A shows the limitations of multi-directional cooling for this application where excessive radial shrinkage causes failure/gap formation. Appendix B contains a result from direct fluxing, i.e., using a metal oxide reducing chemical agent directly on the container, and shows that the agent loses its functionality during the preheating step, which leads to a failure to close the gap. Finally, Appendix C includes steady-state conduction heat transfer results from another student in the MIT Deep Borehole Group to show how much the temperature inside a package can be reduced by closing the gap.

The scientific portion of the work will be published in a journal.
CHAPTER 2. EXPERIMENTAL

2.1. Chapter introduction

The chemicals and the temperature conditions used for the Zn coating process (dry hot-dip galvanizing) and the heating/cooling apparatus used for the filling process is introduced. Sample characterization, thermal resistance measurement, and annealing test method used in the study is also explained.

2.2. Sample preparation

2.2.1. Zn coating

Low carbon steel (AISI 1026) was used as the down-scaled surrogate SNF container (container, hereafter) material. The dimensions of the containers used in the experiment were 2 inch in OD (50.8 mm) with 0.065 inch (1.651 mm) wall thickness and 4 inch (101.6 mm) in height. The containers were galvanized using the conventional dry hot-dip galvanization process that can be found, for example, in a recent review article by Marder [29]. Specifically, they were degreased and pickled, fluxed with a 500 g/L solution of ZnCl₂/NH₄Cl (25:75 wt.%) at 80 °C for 3 minutes, dried at 120 °C for 3 minutes in air, and finally dipped into a bath of zinc with 99.5 wt.% purity. The temperature of the bath was kept around 450 °C and the immersion time was 3 minutes. This gives us a Zn coating
with Fe-Zn intermetallic layers at the steel-coating interface. A picture of the coated tube is shown in Figure 3 with a SEM image showing its cross sectional view.

2.2.2. Heating/cooling apparatus

A custom designed and self-built heating/cooling apparatus was prepared. A schematic of the apparatus is shown in Figure 4-(b). It consisted of a cooling chamber with one inlet and two outlets for water flow. These pipes pass through a thick layer of thermal insulation. The top of the chamber had a socket and a copper chill block was plugged into it to promote directional solidification from the bottom. The head of the block, where the tube was assembled, was coated with graphite to prevent adhesion of the poured melt. The block was replaced after every experiment. A cylindrical radiant heater surrounded the chamber with marginal height to cover the height of the container. A thermal insulation lid with a pouring spout rested on the top of the heater. K-type thermocouples were spot-welded to the outer wall of each container, axially equidistant to each other, to monitor the temperature and control the heater power during sample preparation.

**Figure 3.** Zn-coated container (left) and a SEM image showing the cross sectional view (right).
2.2.3. Experimental test matrix and the filling process

The test matrix is shown in Table 1. Test No.1 is the basis case. The purpose of No.2 and No.3 is to see the effect of the aluminum content and that of No.3 is to see if the process works at lower temperature. Test No.4 uses an uncoated container. The filling procedure is explained as follows based on the temperature-time schematic plot Figure 4-(a). Samples from each test are named based on the format – C: coated and U: uncoated, followed by ZN: Zn filler and ZN4AL: Zn-4wt.%Al filler, and followed by LT: lower filling temperature.

- Preheating: The apparatus was heated up until the top thermocouple started to measure around 400 °C, which is 20 °C lower than the nominal melting point of zinc and 13 °C above the nominal liquidus temperature of Zn-4wt.%Al. The heater power was kept constant at this step. This step required about 30 minutes for the apparatus.
- Oxidation: The heater power was controlled until the three thermocouples started to measure 400 °C. This step required approximately 30 minutes for this apparatus.
- Melt poured: Molten filler, prepared from a separate furnace, was poured into the container through the pour spout. The prepared melt temperature was controlled to match the temperature for the next step.
- Reaction: The heater power was controlled to keep the filler in its liquid state for 10 minutes at 450 °C for test No.1, 2, and 4, and at 400 °C for test No.3.
- Cooling: The heater was turned off and water cooling through the copper chill block started. This forces the solidification front to move unidirectionally-upward from the bottom.

Table 1. Experimental test matrix.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Container</th>
<th>Filler</th>
<th>Filling Temperature (°C)</th>
<th>Procedure</th>
<th>Sample Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zn-coated</td>
<td>Zn</td>
<td>450</td>
<td>(b)-(c)-(d)</td>
<td>CZN</td>
</tr>
<tr>
<td>2</td>
<td>Zn-coated</td>
<td>Zn-4wt.%Al</td>
<td>450</td>
<td>(b)-(e)-(f)-(g)-(d)</td>
<td>CZN4AL</td>
</tr>
<tr>
<td>3</td>
<td>Zn-coated</td>
<td>Zn-4wt.%Al</td>
<td>400</td>
<td>(b)-(c)-(d)</td>
<td>CZN4ALLT</td>
</tr>
<tr>
<td>4</td>
<td>Uncoated</td>
<td>Zn-4wt.%Al</td>
<td>450</td>
<td>(b)-(e)-(f)</td>
<td>UZN4AL</td>
</tr>
</tbody>
</table>
2.3. Characterization

CZN, CZN4AL and CZN4ALLT were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), referred to as the experimental procedure (d) in Figure 4. All samples were processed based on the test matrix (Table 1) and the illustration shown in Figure 4 prior to the analyses. Specifically, for CZN and CZN4ALLT, the part between the top and the middle thermocouple was kept and the remainder below the cut was archived. The surfaces were first flattened using a lathe and then they were ground and polished to 1 μm. The bottom part of the post-processed samples was characterized. CZN4AL was prepared using the same process but after the thermal resistance measurement step, which is explained next. The SEM model used in the study was FEI/Philips XL30 Feg ESEM and the EDX software used was TEAM™ EDS developed by EDAX.

2.4. Thermal resistance measurement

CZN4AL and UZN4AL were used for thermal resistance measurement and comparison. For the measurement, the samples were sectioned at the height where the top and the bottom thermocouples were located during the filling process and the surfaces were flattened using a metal working tool. An axially oriented hole was drilled at the center of each sample and a cartridge heater with a built-in K type thermocouple was inserted. A silver paste was applied to the surface of the heater to minimize the contact resistance between the heater and the filler. Four thermocouples were attached to the container wall, angularly equidistant to each other at a fixed axial height of approximately mid height, to take the error of heater placement asymmetry into account. The power of the heater was incrementally increased by 10 W from 20 W to 100 W. The container wall was cooled with forced convection of air and the top and the bottom of the samples were thermally insulated. The measurements continued until the temperature increase reached an asymptote at each power step and the quasi-steady-state temperature value was taken for the effective thermal conductivity calculation using Fourier’s law of conduction, which will be shown in Chapter 3.2. The process is illustrated in the experimental procedure (e) and (f) of Figure 4. The data logger used for the measurement was an Agilent Technologies 34980A and the software used was 34980A Benchlink Data Logger Software v.2.3.0. The DC power supply used for the heater was Chroma model 62050P-100-100.
2.5. Annealing

After the initial characterization, CZN, CZN4AL, and CZN4ALLT were annealed to observe the phase growth in the sample. The purpose of the test is explained in Chapter 3.6. The process went on inside a box furnace filled with air for 24 hours and then for 96 hours, thus 5 days in total. The samples were mounted on top of a heat insulating stage. The temperature in the furnace was increased from room temperature to 300 °C with an increment of 10 °C per minute. The time count started after the temperature reached 300 °C. The cooling process was also gradual, taking the samples out from the furnace to room temperature air while the bottom was insulated. After cooling down, the surface was polished to remove oxides before examination.
Figure 4. A schematic of the experimental procedure.
CHAPTER 3. RESULTS AND DISCUSSION

3.1. Chapter introduction

The measured temperature results from the filling process and the images of the samples after the post-processing steps are shown in Figure 5 through Figure 8. The container-filler interfacial gap was completely closed in CZN4AL and CZN4ALLT and completely opened in UZN4AL. In CZN, the gap was closed but a crack was formed at the region near the interface. In CZN4AL, dark grayish morphology was observed near the interface. The characterization results of this area showed that these are rich in Al. Table 2 tabulates the observations. The subsequent sections show the results with detailed discussion based on a question and answer format.

Table 2. The naked eye observation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZN</td>
<td>Gap closed. Crack near the container/filler interface.</td>
</tr>
<tr>
<td>CZN4AL</td>
<td>Gap closed. Grayish morphology near the container/filler interface.</td>
</tr>
<tr>
<td>CZN4ALLT</td>
<td>Gap closed.</td>
</tr>
<tr>
<td>UZN4AL</td>
<td>Gap opened.</td>
</tr>
</tbody>
</table>
Figure 5. Measured temperature plots from the filling process of test No.1 (up) and the images of CZN after the post-processing steps (down).
Figure 6. Measured temperature plots from the filling process of test No.2 (up) and the images of CZN4AL after the post-processing steps (down).
Figure 7. Measured temperature plots from the filling process of test No.3 (up) and the images of CZN4ALLT after the post-processing steps (down).
Figure 8. Measured temperature plots from the filling process of test No.4 (up) and the images of UZN4AL after the post-processing steps (down).
3.2. Q1: How much did thermal conductivity improve by closing the gap?

3.2.1. Thermal resistance measurement result

The temperatures from the thermal resistance measurement experiment are shown in Figure 9. As mentioned earlier in Chapter 2.3, the quasi-steady-state temperatures were taken at each step. Here, we assumed that the built-in thermocouple measured the surface temperature of the heater. Comparing the result from CZN4AL and UZN4AL, not only the difference in the heater surface temperatures is visible but also the differences between those and each wall temperature are significant. The notable difference amongst the four wall temperatures of UZN4AL is caused by the asymmetrically located filler block in the container due to the open gap.

For a better comparison, effective thermal conductivity (ETC) of the two samples was calculated using the measured temperature data. In the calculation, it was assumed that the heater power was axially uniform, i.e., \( q' = \dot{Q} / L \) where \( \dot{Q} \) is the measured electrical input power and \( L \) is the length of the heater, and the system had angular symmetry, and therefore, the one-dimensional (in radial direction) steady-state heat conduction equation for the cylindrical coordinates, i.e.,

\[
ETC = \frac{q' \ln \left( \frac{R_{container, OD}}{R_{heater, OD}} \right)}{2\pi (T_{heater, surface} - T_{wall})}
\]

was used. ETCs were calculated using the heater surface temperature with each wall temperature and were averaged and plotted in Figure 10. The data points are the averaged values and the error bars are the standard deviations of the four ETC values. The results were very sensitive to the input radius. Thus, not only the uncertainties associated with the temperature measurements but also the positional uncertainties, e.g., uncertainty from taking the built-in thermocouple as the heater surface temperature, caused the difference between the ETC of CZN4AL and the nominal ETC, i.e., ETC from nominal thermal conductivity of low carbon steels and Zn, without the gap. Therefore, the values should not be directly used in further studies, e.g., in heat transfer calculations. However, relative comparison of the two ETC is acceptable since they were measured/calculated in the same experimental condition and the same assumptions. Based on the results, closing the gap increased the ETC by about a factor of 6.
Figure 9. Raw temperature data measured from (a) UZN4AL and (b) CZN4AL.

Figure 10. Effective thermal conductivity comparison between CZN4AL and UZN4AL.
3.2.2. Answer to the question

**Q1: How much did thermal conductivity improve by closing the gap?**

**- Answer -**

Using a Zn coated container with Zn/Zn-4Al can close the container-filler interfacial gap and the effective thermal conductivity increased by a factor of 6 under the experimental condition.

3.3. Q2: What happens if we use pure Zn filler?

3.3.1. Characterization result of CZN

The backscattered SEM images (Figure 11) from CZN, where Zn was used as the filler, showed that the distinguishable layered morphology of Fe-Zn intermetallic compounds that was present in the Zn coating mostly disappeared after the filling process. Instead, the phases were detached and stayed as inclusions in the Zn filler region.

For a better view, an SEM image is also shown in Figure 12. Most of the dark spots in the image are pores filled/contaminated with SiO$_2$ grit paper particles and polishing suspensions, based on point EDX analysis where it showed Zn and Si/O. The dark grayish spots such as those denoted with arrows are Fe-Zn intermetallic compounds.

3.3.2. Disadvantages of using pure Zn

The characterization result of CZN did not show the distinctive layered structure of the Fe-Zn intermetallic phases that as-produced galvanized coatings have, for example, as it is shown in the right image of Figure 3. However, regional separation of Fe and Zn is thermodynamically unstable and the two will continue to mix until it reaches equilibrium, forming several layers of Fe-Zn intermetallic phases, i.e., $\Gamma$ (Fe$_3$Zn$_{10}$), $\Gamma'_1$ (Fe$_{11}$Zn$_{40}$), $\delta_{1k}$ (FeZn$_7$), $\delta_{1p}$ (FeZn$_{10}$), and $\zeta$ (FeZn$_{13}$), from the Fe/steel side to the Zn side. Note that the $\delta_{1k}$ and $\delta_{1p}$ phase is sometimes combined and denoted...
as $\delta_1$ or just $\delta$ phase, depending on articles. A binary phase diagram of the Fe-Zn system is attached here for reference (Figure 13).

From a practical point of view, disposal packages will be exposed at a high enough temperature where the reaction kinetics of the Fe-Zn formation, i.e., dissolution and diffusion of Fe into Zn and diffusion of Zn into Fe/steel, can speed up. Any post-filling processes such as container lid welding or annealing for residual stress relief can be examples. More importantly, the radioactive decay heat and low thermal conductance of host rocks will contribute to the process by increasing the temperature of the package, and therefore, the temperature of the Zn filler over the long term.

Kinetics studies on the growth of the Fe-Zn layers via solid state diffusion are available in the literature. Short term (less than an hour) [31] and long term (from 1 to 30 hours) [32] growth rates of Fe-Zn at 400 °C were reported by Syahbuddin and Munroe where diffusion coupled samples of pure Fe and pure Zn were used. Their results showed that the growth rate started to follow a parabolic law after 3 hours. Growth rates of Fe-Zn at lower temperatures were reported by Onishi et al [33] where they used Fe, electroplated with Zn. Their temperature condition ranged from 240 to 410 °C but the growth rate plots are only available for 300, 340, and 380 °C. The thickness of the layer was on the order of 100 $\mu$m even after a couple of days of heat treatment and the parabolic law was not observed.

Figure 11. Backscattered SEM images taken at the interface between the Zn filler and the low carbon steel container of CZN.
Figure 12. SEM image from CZN. The arrows denote Fe-Zn intermetallic phases. The dark spots are pores filled with grit paper particles or polishing suspensions.

From the available information, we can expect that Fe-Zn layers with significant thickness will form at the container-filler interface if we use pure Zn as a filler. Usually, these layers are undesired in galvanizing mostly because of mechanical reasons. Significant residual stresses develop during the formation of each Fe-Zn phase layer and during phase transformation from one to another due to the difference in specific volumes [34], caused by the difference in stoichiometry and crystal structures. Residual stresses also arise from thermal strain, caused by the difference in thermal expansion coefficient [35], which leads to, for example, the as-produced micro-cracks formed in the δ phases [36]. See Table 3 for crystal structure and relevant physical and mechanical properties of each phase. The micro-cracks directly contribute to the failure of galvanized coating under the presence of external stresses. Detailed explanation of the cracking mechanisms can be found
elsewhere [36]–[40]. In a Zn filled disposal package, such cracks will play the role of secondary gaps, increasing thermal resistance. At this point, we can claim the following:

- The expected temperature in the disposal package will be high enough to promote the growth of the Fe-Zn phases.
- According to the literature, parabolic growth was not observed at the relatively low annealing temperature and the thickness of the phase layer was on the order of ~100 µm even after a couple of days of annealing. Even if the growth rate follows the parabolic law, a significant thickness of a Fe-Zn phase layer will easily form between the disposal container and the Zn filler.
- Cracks can initiate and propagate in the Fe-Zn phase layers by impacts during transportation, storage, and emplacement and this can increase thermal resistance.
- In the long run, the process will continue and the thickness of the container will be reduced while that of the Fe-Zn phase layer increases. This can embrittles the container by increasing the volume of Fe-Zn while decreasing the volume of the container material.

3.3.3. Answer to the question

Q2: What happens if we use pure Zn?

- Answer -

Using pure Zn as a void filler while the gap is closed leads to the growth of the mechanically undesired Fe-Zn phases at the interface, hence should be avoided.
Figure 13. Fe-Zn phase diagram by Nakano et al [30] from the ASM Alloy Phase Diagram Database™.

Table 3. Crystal structure and properties of interest of the Fe-Zn intermetallic compounds.

<table>
<thead>
<tr>
<th>Phase</th>
<th>( \alpha ) (Fe)</th>
<th>( \Gamma ) (Fe(<em>3)Zn(</em>{10}))</th>
<th>( \Gamma_1 ) (Fe(<em>5)Zn(</em>{21}))</th>
<th>( \delta ) (FeZn(_{10}))</th>
<th>( \zeta ) (FeZn(_{13}))</th>
<th>( \eta ) (Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure [41]</td>
<td>BCC</td>
<td>BCC</td>
<td>FCC</td>
<td>Hexagonal</td>
<td>Monoclinic</td>
<td>HCP</td>
</tr>
<tr>
<td>Thermal expansion coefficient ((10^{-6}/\text{K})) [35]</td>
<td>21.78</td>
<td>23.10</td>
<td>29.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>210</td>
<td>140 (( \delta_{1p} ))</td>
<td>117</td>
<td>75</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4. **Q3: Can we suppress the formation of the Fe-Zn intermetallic phases?**

3.4.1. *From the literature*

Whenever two or more dissimilar metals are in contact, they mix to lower the thermodynamic potential of the system. Depending on the combination of elements, they either stay as a mixture or form intermetallic compounds. Such behavior is inevitable in this application since the aim of the method is to allow metallic bonding between the container and the filler, and therefore, the two will be in direct contact. However, this inevitability can be bypassed by providing a diffusion barrier by adding alloying elements to the filler that preferentially form intermetallic phases that are relatively desirable.

A good example of this method is adding a minor amount of Al into a bath of Zn in galvanizing. The Al content in the bath, typically around 0.2 wt.%, preferentially forms Fe-Al intermetallic phases with the dissolved Fe from the steel which delays the formation of the Fe-Zn phases [42]. Generally, Fe-Al is more desirable than Fe-Zn due to its higher work of adhesion towards Fe/steel [43][44]. Moreover, unlike Fe-Zn, where several phases form of which each has different properties as discussed earlier, one phase (Fe$_2$Al$_5$) dominates among the Fe-Al phases at the Fe/Zn-0.2wt.%Al interface [42]. However, it is known that the Fe-Al eventually transforms into Fe-Zn when the composition of Al in the bath is low, e.g., 0.2 wt.%. More importantly, it was reported that having such a temporary inhibition layer speeds up the growth of Fe-Zn during annealing at 400 °C [32]. It is unknown if such behavior will also occur at lower temperatures but if it does, having minor content of Al in the filler would be worse than using pure Zn.

3.4.2. *Answer to the question*

---

**Q3: Can we suppress the formation of the Fe-Zn intermetallic phases?**

- **Answer** -

The formation of the Fe-Zn intermetallic phases can be suppressed by adding Al to Zn, however, the resulting Fe-Al intermetallic phases can be destabilized when the Al content in Zn is too low.
3.5. Q4: How much Al do we need to prevent Fe-Al/Fe-Zn transformation?

3.5.1. The mechanism of the Fe-Al/Fe-Zn transformation.

Two models were proposed to explain the Fe-Al/Fe-Zn transformation. One is the Al-depletion model [45] and the other is the Zn-diffusion model [46]. The Al-depletion model explains that the formation of Fe-Al leads to local depletion of Al near the region and the resulting compositional change switches the stable intermetallic phase from Fe$_2$Al$_5$ to the $\delta_1$. The model is illustrated in the Fe-Al-Zn ternary phase diagram in Figure 14. The Zn-diffusion model explains that the transformation is due to the diffusion of Zn from the bath, through the Fe-Al layer, to the steel, forming Fe-Zn intermetallics in the region adjacent to the steel. Thus, the nucleation site of Fe-Zn should be in between the Fe-Al layer and the Zn bath if the Al-depletion model is correct and it should be in between the steel and the Fe-Al layer if the Zn-diffusion model is correct. For better understanding, an illustration is shown in Figure 16.

Based on the two models, Adachi et al [47] and Kato et al [48] used a galvanizing-galvannealing method to further study the phase transformation. The composition of the galvanizing bath they used was Zn-0.2Al in weight percent and the dipping time was short enough to prevent the transformation during the galvanizing stage. Despite their same experimental condition, the two studies did not support the same model. The study by Adachi et al [47] tend to follow the Zn-diffusion model, where they observed Fe-Zn intermetallic formed at the Fe/Fe-Al interface. They explained the phase transformation by claiming that the growth of Fe-Zn mechanically destabilizes the Fe-Al, detaching it from the steel. However, the more recent study by Kato et al [48] disagreed with the Zn-diffusion model by observing the Fe-Zn intermetallics formed at the Fe-Al/Zn-Al interface. In addition, Kato’s study questioned the Al-depletion model after observing the $\zeta$ phase instead of the $\delta_1$ phase, which is the expected phase to be formed according to the model, and detecting no depletion of Al in Zn-Al near the Fe-Al/Zn-Al interface.

An article by Park et al [49] explains the phenomenon observed by Kato et al. Based on their parametric study, i.e., varying reaction time, they claimed that the local depletion of Al leads to the formation of the $\zeta$ phase, which again transforms to the $\delta$ phase by the homogenization of Al by its influx from the surroundings. Figure 15 provides an illustration of this process. Such homogenization of Al was also mentioned in the earlier study by Guttmann [46].
Figure 14. Ternary phase diagram of Fe-Al-Zn by Nakano et al [50] from the ASM Alloy Phase Diagram Database™. The annotations explain the Al-depletion model. Depletion of Al switches the composition along the direction of the blue arrow to the blue triangle region where $\delta_1$, $\eta(Zn)$, and $Zn_8FeAl$ coexists.

Figure 15. Ternary phase diagram of Fe-Al-Zn by Nakano et al [50] from the ASM Alloy Phase Diagram Database™. The annotations explain Al depletion followed by Al diffusion. Depletion of Al switches the composition along the direction of the green arrow to the two phase region of $\zeta$ and $\eta(Zn)$. Diffusion of Al from the surroundings again switches the composition along the direction of the blue arrow to the blue triangle region where $\delta_1$, $\eta(Zn)$, and $Zn_8FeAl$ coexists.
In summary, more studies tend to show agreement with the Al-depletion model. Dissolution of Fe into liquid Zn-Al leads to the formation of Fe-Al and this causes local depletion of Al in the adjacent regions, resulting in the formation of Fe-Zn intermetallic. However, the concentration gradient of Al becomes homogenized by diffusion of Al and this switches the stable phase to the $\delta_1$ phase. Thus, we can deduce that the key to prevent the phase transformation is to avoid such local depletion. Then, how much Al do we need?

![Figure 16](image)

**Al depletion model**

**Zn diffusion model**

*Figure 16.* Illustration of the nucleation of Fe-Zn based on the Al depletion model (left) and the Zn diffusion model (right).

### 3.5.2. Minimal required amount of Al to prevent Fe-Al/Fe-Zn transformation

We continue the discussion using the same Fe-Al-Zn ternary phase diagram. In Figure 17, zone 1 is the region where Fe-Al intermetallic(s) is(are) stable while Fe-Zn intermetallic(s) is(are) not. Zone 2 is the region where both Fe-Al and Fe-Zn intermetallics are stable. The remainder is the region where Fe-Al intermetallics are unstable. Thus, to prevent the transformation the composition of the three elements should always reside in zone 1. It is known from a highly cited study by Kobayashi et al. [51] that the formation of Fe-Al is controlled by the diffusion of Fe through the preformed Fe-Al layer. This means that Fe atoms will hardly be observed in the Al depleted region (ADR) because they will be consumed by the formation of Fe-Al. Thus, the composition of ADR will reside very close to the Al-Zn boundary in the ternary phase diagram. If the composition of Al in ADR becomes lower than the limit denoted by the line A, i.e., above the line A, Fe-Zn intermetallics will form.
Further transformation depends on how much Al diffuses into that ADR. If the composition of Al in ADR becomes higher than the limit denoted by the line B, i.e., below the line B, Fe-Al will be the only stable intermetallic(s). Here, there is also about 5 at.% of Fe-Al stability margin thus Fe-Al/Fe-Zn transformation is very unlikely to occur. The characterization results of CZN4AL and CZN4ALLT in the subsequent sections give examples.

Figure 17. Ternary phase diagram of Fe-Al-Zn by Nakano et al [50] from the ASM Alloy Phase Diagram Database™. The composition ranges of interest are marked.
3.5.3. Characterization result of CZN4AL

As shown in the backscattered SEM image in Figure 19, thick layers of Fe-Al intermetallic phases (the dark areas) were formed in CZN4AL. This morphology is similar to that from steel samples dipped into liquid Zn-Al with eutectic composition, i.e., Zn with 5 weight percent of Al. Example images can be found, for example, in the articles by Chen et al [52]. Looking at the figure, Fe-Al is densely formed at the steel/Fe-Al interface but it becomes sparse as it goes into the interior. Atomic compositions at several points were measured using point EDX analysis. The points are marked on the SEM image shown in Figure 19 and each composition is tabulated in Table 4. The acceleration voltage used in the analysis was 15 kV and the measurement was performed for 30 seconds per point while the number of counts per second was around 30 k. In the table, only the Fe-Al stoichiometry is concerned since the beam may have covered the Zn-rich phase that was surrounding the phases of
interest or Zn could have been mixed into the Fe-Al phases. The Fe-Al phase close to the steel/Fe-Al interface had higher composition of Fe and the stoichiometry was close to Fe$_2$Al$_5$. However, the Fe-Al phase apart from the interface had a lower composition of Fe and the stoichiometry was close to FeAl$_3$. A recent Fe-Al binary phase diagram is shown in Figure 18 for reference. Note that Fe$_2$Al$_5$ is denoted as Fe$_4$Al$_{13}$ and FeAl$_3$ is denoted as FeAl$_{2.8}$ in the diagram.

Figure 19. Backscattered SEM images of CZN4AL. Spots where point EDX analysis was performed are marked with bracketed alphabet. The zoomed-in images are magnified 1200 times.
Table 4. Atomic compositions obtained from point EDX analysis of CZN4AL.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Al at.% (error %)</th>
<th>Fe at.% (error %)</th>
<th>Zn at.% (error %)</th>
<th>Al/Fe*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A – (a)</td>
<td>64.28 (5.42)</td>
<td>25.18 (3.05)</td>
<td>10.54 (5.63)</td>
<td>2.56 ± 0.22</td>
</tr>
<tr>
<td>A – (b)</td>
<td>64.39 (5.43)</td>
<td>24.67 (3.06)</td>
<td>10.94 (5.61)</td>
<td>2.62 ± 0.22</td>
</tr>
<tr>
<td>A – (c)</td>
<td>66.52 (5.22)</td>
<td>25.28 (3.00)</td>
<td>8.20 (6.27)</td>
<td>2.64 ± 0.22</td>
</tr>
<tr>
<td>B – (a)</td>
<td>66.06 (5.28)</td>
<td>24.94 (3.01)</td>
<td>9.00 (5.91)</td>
<td>2.66 ± 0.22</td>
</tr>
<tr>
<td>B – (b)</td>
<td>66.54 (5.21)</td>
<td>25.49 (2.99)</td>
<td>7.97 (6.26)</td>
<td>2.62 ± 0.21</td>
</tr>
<tr>
<td>C – (a)</td>
<td>71.21 (4.84)</td>
<td>23.34 (2.98)</td>
<td>5.45 (7.22)</td>
<td>3.06 ± 0.24</td>
</tr>
<tr>
<td>C – (b)</td>
<td>71.45 (4.79)</td>
<td>23.84 (2.98)</td>
<td>4.71 (8.24)</td>
<td>3.00 ± 0.23</td>
</tr>
<tr>
<td>D – (a)</td>
<td>71.81 (4.78)</td>
<td>23.35 (2.99)</td>
<td>4.84 (7.67)</td>
<td>3.08 ± 0.24</td>
</tr>
<tr>
<td>D – (b)</td>
<td>70.78 (5.04)</td>
<td>20.17 (3.13)</td>
<td>9.05 (5.79)</td>
<td>3.52 ± 0.29</td>
</tr>
<tr>
<td>E – (a)</td>
<td>71.45 (4.91)</td>
<td>21.43 (3.05)</td>
<td>7.12 (6.41)</td>
<td>3.34 ± 0.27</td>
</tr>
<tr>
<td>F – (a)</td>
<td>72.73 (4.74)</td>
<td>22.19 (3.01)</td>
<td>5.07 (7.50)</td>
<td>3.29 ± 0.25</td>
</tr>
</tbody>
</table>

* The Al/Fe of Fe2Al5 is 2.5 and that of FeAl3 is 3.

3.5.4. Characterization result of CZN4ALLT

From the naked eye view in , Fe-Al (dark areas) was not visible in CZN4ALLT. However, as shown in the backscattered SEM image in Figure 20, a minor amount of Fe-Al was formed at the interface. Note the difference in image magnifications between these images (x500/x5000) and those of CZN4AL (x120/x1200). Minor breakaway of Fe-Al was also observed and the point EDX analysis showed the same result – closer composition to Fe2Al5 at the interface and to FeAl3 as it goes into the interior. The point EDX analysis was performed under the same condition as CZN4AL. The target spots are marked in Figure 20 and the atomic compositions are tabulated in Table 5.
Figure 20. Backscattered SEM images of CZN4ALLT. Spots where point EDX analysis was performed are marked with bracketed alphabet. The zoomed-in images are magnified 5000 times.

Table 5. Atomic compositions obtained from point EDX analysis of CZN4ALLT.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Al</th>
<th>Fe</th>
<th>Zn</th>
<th>Al/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at.%</td>
<td>at.%</td>
<td>at.%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(error %)</td>
<td>(error %)</td>
<td>(error %)</td>
<td></td>
</tr>
<tr>
<td>A – (a)</td>
<td>72.67 (4.64)</td>
<td>22.61 (3.02)</td>
<td>4.72 (8.25)</td>
<td>3.22 ± 0.25</td>
</tr>
<tr>
<td>B – (a)</td>
<td>73.24 (4.56)</td>
<td>22.96 (3.01)</td>
<td>3.81 (9.47)</td>
<td>3.20 ± 0.24</td>
</tr>
<tr>
<td>B – (b)</td>
<td>72.44 (4.63)</td>
<td>23.17 (3.01)</td>
<td>4.39 (8.21)</td>
<td>3.13 ± 0.24</td>
</tr>
<tr>
<td>B – (c)</td>
<td>72.14 (4.62)</td>
<td>24.08 (2.97)</td>
<td>3.78 (8.83)</td>
<td>3.00 ± 0.23</td>
</tr>
<tr>
<td>B – (d)</td>
<td>70.97 (4.68)</td>
<td>25.44 (2.95)</td>
<td>3.59 (9.85)</td>
<td>2.80 ± 0.21</td>
</tr>
</tbody>
</table>

* The Al/Fe of Fe$_2$Al$_5$ is 2.5 and that of FeAl$_3$ is 3.
3.5.5. EDX mapping result and discussion

Element mapping results of CZN4AL and CZN4ALLT are shown in Figure 21. The mapping resolution was 1240 by 800 and it was scanned 32 times with 100 microseconds of dwelling time. This took around 1 hour per sample. The acceleration voltage was 15 kV and the number of counts per second was around 70 k. The mapping was performed separately from the point EDX analysis. Thus, the region shown in the map does not match the region used for the point analysis.

No notable trace of Fe-Al/Fe-Zn transformation was found both in CZN4AL and CZN4ALLT. Comparing each element mapping, the Fe rich areas match the Al rich areas which also matches the Zn depleted areas. The time for Al atoms to reach the dissolved Fe atoms was shorter in CZN4AL because of the high temperature condition, which was enough to melt the Zn layer inside the ZnO layer, promoting the detachment of the oxide. Thus, the reaction time was longer in CZN4AL which resulted in more Fe-Al at and near the interface. Based on the observations, 4 weight percent of Al in Zn was enough to prevent Fe-Al/Fe-Zn transformation under the experimental condition.

3.5.6. Answer to the question

Q4: How much Al do we need to prevent Fe-Al/Fe-Zn transformation?

- Answer -

To prevent the Fe-Al/Fe-Zn transformation, the Al composition in the Al depleted region should be high enough, not to cross the line A in Figure 17. CZN4AL and CZN4ALLT results showed that 4 weight percent of Al was enough.
Figure 21. EDX mapping results from CZN4AL and CZN4ALLT. The mapping resolution is 1240 by 800 and it was scanned 32 times with 100 microseconds of dwelling time. This took around 1 hour per sample. The acceleration voltage was 15 kV and the number of counts per second was around 70 k. Larger images of each element mapping are shown in Appendix D.
3.6. Q5: Will Fe-Al/Fe-Zn transformation occur after solidification?

3.6.1. The problem

The key to prevent the Fe-Al/Fe-Zn transformation was to keep the composition of each element in Al depleted regions to reside in zone 1 in Figure 17. Unlike the liquid phase, Zn-Al separates into Zn rich and Al rich phases after solidification. According to the binary phase diagram of the Al-Zn system, the composition of Al in the Zn rich phase is around 1 atomic percent at the highest expected temperature (around 150 °C) inside a disposal package (see Appendix C), as it is annotated with red in Figure 24. This is beyond zone 1 in Figure 17 and above the line A, where Fe-Al/Fe-Zn transformation can occur.

Despite the abundant articles related to Fe-Al and Fe-Zn intermetallics, none of them provide a direct answer to this question. This is because we are interested in an extremely long term behavior at a low temperature while the majority of the studies aim at short term behavior at high temperatures to promote diffusion. To the author’s knowledge, the lowest temperature condition for solid state kinetics of Fe-Zn is 240 °C [33] and that of Fe-Al is 440 °C [54]. Due to this reason, short term annealing tests were performed with CZN4AL and CZN4ALLT based on the process explained in Chapter 2.5.

3.6.2. Annealing test results

Optical microscope images taken at the same spot of each sample prior to annealing, after 24 hours, and after 5 days are shown in Figure 22. Notable changes were not observed in both samples even after 5 days of annealing at 300 °C. Point EDX analysis was also performed at several spots in CZN4AL. The spots are marked at the SEM image in Figure 23 and the atomic composition at each spot is tabulated in Table 6. The same settings that were used in the previous chapter were used for the analysis but the oxidized sample was directly used without polishing since the oxide thickness was negligible (EDX did not detect oxygen). Neither this result showed any difference – Fe-Al at the interface being close to Fe$_2$Al$_5$ and that at the interior being close to FeAl$_3$.

Predicting the long term behavior is left as a future study. The temperature inside the disposal package might be not enough to overcome the activation energy of the Fe-Al reaction or its kinetics can be extremely slow.
Figure 22. Optical microscope images with 5 times magnification of CZN4AL and CZN4ALLT prior to annealing, and after 24 hours and after 5 days of annealing.
Figure 23. SEM images of CZN4AL after 5 days of annealing. Spots where point EDX analysis was performed are marked with bracketed alphabet.

3.6.3. Answer to the question

Q5: Will Fe-Al/Fe-Zn transformation occur after solidification?

- Answer -

CZN4AL and CZN4ALLT did not show any noticeable difference in micro-scale after 5 days of annealing at 300 °C. Further studies are required to answer this question.
Table 6. Atomic compositions obtained from point EDX analysis of CZN4AL after 5 days of annealing.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Al at.% (error %)</th>
<th>Fe at.% (error %)</th>
<th>Zn at.% (error %)</th>
<th>Al/Fe*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A – (a)</td>
<td>73.61 (4.52)</td>
<td>23.74 (2.92)</td>
<td>2.65 (12.44)</td>
<td>3.11 ± 0.23</td>
</tr>
<tr>
<td>A – (b)</td>
<td>73.35 (4.61)</td>
<td>22.53 (2.96)</td>
<td>4.12 (8.20)</td>
<td>3.26 ± 0.25</td>
</tr>
<tr>
<td>B – (a)</td>
<td>73.93 (4.54)</td>
<td>22.70 (2.95)</td>
<td>3.38 (9.06)</td>
<td>3.26 ± 0.24</td>
</tr>
<tr>
<td>B – (b)</td>
<td>73.79 (4.56)</td>
<td>22.66 (2.95)</td>
<td>3.54 (9.42)</td>
<td>3.26 ± 0.24</td>
</tr>
<tr>
<td>C – (a)</td>
<td>72.49 (4.64)</td>
<td>23.92 (2.93)</td>
<td>3.58 (9.08)</td>
<td>3.04 ± 0.23</td>
</tr>
<tr>
<td>C – (b)</td>
<td>73.27 (4.59)</td>
<td>23.11 (2.95)</td>
<td>3.63 (9.43)</td>
<td>3.18 ± 0.24</td>
</tr>
<tr>
<td>D – (a)</td>
<td>71.43 (4.68)</td>
<td>25.62 (2.92)</td>
<td>2.96 (12.89)</td>
<td>2.79 ± 0.21</td>
</tr>
<tr>
<td>D – (b)</td>
<td>71.43 (4.76)</td>
<td>23.76 (2.96)</td>
<td>4.81 (7.71)</td>
<td>3.01 ± 0.23</td>
</tr>
<tr>
<td>D – (c)</td>
<td>72.41 (4.64)</td>
<td>24.18 (2.93)</td>
<td>3.41 (8.99)</td>
<td>3.00 ± 0.23</td>
</tr>
<tr>
<td>D – (d)</td>
<td>69.77 (4.89)</td>
<td>24.66 (2.96)</td>
<td>5.57 (7.21)</td>
<td>2.84 ± 0.22</td>
</tr>
<tr>
<td>D – (e)</td>
<td>70.63 (4.84)</td>
<td>24.08 (2.97)</td>
<td>5.29 (7.72)</td>
<td>2.94 ± 0.23</td>
</tr>
<tr>
<td>D – (f)</td>
<td>71.21 (4.75)</td>
<td>24.52 (2.94)</td>
<td>4.27 (7.79)</td>
<td>2.91 ± 0.22</td>
</tr>
</tbody>
</table>

* The Al/Fe of Fe$_2$Al$_5$ is 2.5 and that of FeAl$_3$ is 3.
3.7. Q6: What would be the adequate composition of Al?

3.7.1. Practical point of view

Increasing the Al composition beyond the eutectic point increases the liquidus temperature. Thus, the required temperature for the filling process will increase. The tolerance limit of the materials in the SNF from a fast spectrum reactor, i.e., ferritic/martensitic steels, while in contact with liquid Zn-Al is currently unknown. However, since the solubility generally increases with temperature, the processing temperature should be kept as low as possible. For reference, liquid metal corrosion test results on a non-irradiated 316L steel in a liquid Zn-Al bath with varying composition of Al are included in an article by Liu et al. [56]. Their results showed that the thickness loss of the steel was negligible when it was dipped into liquid Zn-0.18wt.%Al at 460 °C and into liquid Zn-5wt.%Al at 490 °C but was observable when it was dipped into liquid Zn-55wt.%Al at 600 °C after 10 days. Liquid metal corrosion of irradiated ferritic/martensitic steels in liquid Zn-Al remains as a future study.

3.7.2. Kinetics point of view

Although the Fe-Al intermetallics are preferred to the Fe-Zn intermetallics, their formation also causes the loss of Fe from the container. Using a near eutectic Zn-Al allows us to do the filling process below the melting point of Zn, which is the base material of the coating on the container. The result of CZN4ALLT showed that it can also successfully close the container-filler interfacial gap while delaying the growth of the Fe-Al intermetallics. Besides the lower diffusivity due to the lower temperature, the delay is likely to be caused by the ZnO layer, providing a diffusion barrier for Al atoms to reach the steel side. This was not the case in CZN4AL since the filling temperature was 450 °C, which is above the nominal melting point of pure Zn (420 °C), promoting the detachment of the ZnO diffusion barrier by melting the basis Zn layer.

3.7.3. The lower limit

It was claimed previously that the composition of Al should be higher than the Fe-Al/Fe-Zn transformation limit. However, assuming such transformation occurs even after solidification, the
composition of Al should be even higher than the lower limit, which is marked with green color in Figure 24. This is because the solidified structure will be composed of the primary Zn rich phase if the composition is below that limit because the cooling rate will be too fast to allow phase separation. Note that the phase separation can be preferred due to the resulting lamellar structure of the Zn rich and the Al rich phases – the Al depleted region can recover Al more easily due to the short diffusion distance.

3.7.4. *Hyper-eutectic vs. hypo-eutectic*

Having a slightly hyper-eutectic (to the right from the eutectic point) or slightly hypo-eutectic (to the left from the eutectic point) composition will eventually make no big difference on the ratio between Zn rich and Al rich phases when it reaches equilibrium. However, the eutectic point of the Al-Zn system is very closely located to the Zn side. Especially, the sudden shift of the Al composition in the Al rich phase accompanied by a rapid cooling rate will make the system far from equilibrium. The solidification structure of hyper-eutectic Zn-Al will consist of primary Zn rich islands with Zn rich and Al rich lamella structure. Thus, the sudden shift in Al only affects the lamella structure. Conversely, the solidification structure of hypo-eutectic Zn-Al will consist of primary Al rich islands with Zn rich and Al rich lamella structure. Thus, the sudden shift in Al affects both the islands and the lamella structure. Comparing the two and determining which one is superior to the other require kinetic studies at the microscopic level. Thus, it is not covered here but recommend as one of the future studies.

3.7.5. *Answer to the question*

**Q6: What would be the adequate composition of Al?**

- **Answer** -

Using a near eutectic Zn-Al allows us to do the filling process at a lower temperature. The benefits from this are twofold. First, the corrosion rate decreases. Second, it keeps the ZnO diffusion barrier, which delays the growth of the Fe-Al intermetallic phases.
Figure 24. Al-Zn phase diagram by Okamoto [55] from the ASM Alloy Phase Diagram Database™. The red annotation is for section 3.6.1, the green annotation is for section 3.7.3, and the blue annotation is for section 3.7.4.
CHAPTER 4. CONCLUDING REMARKS

4.1. Work summary and conclusions

The approach of improving heat transfer inside spent nuclear fuel disposal packages by means of metallic void fillers was introduced. Coating the disposal container with a slowly oxidizing metal was suggested to maximize its thermal benefit. This helps closing the container-filler interfacial gap, which otherwise significantly increases the thermal resistance of the package, by promoting metallic bonding between the two. Zn-coated low carbon steel containers with Zn and Zn-4wt.%Al void filler were tested in this study. The interfacial gap was completely closed when the Zn-Al filler was used and this increased the effective thermal conductivity by a factor of 6, compared to an uncoated container, under the same experimental conditions. Metallurgical aspects were discussed in detail using a question and answer format based on SEM/EDX analyses and literature reviews. Based on the answers to the questions, the following conclusions can be made.

- Using pure Zn as a void filler, while the gap is closed, leads to the growth of mechanically undesired Fe-Zn phases at the interface, hence should be avoided.
- The formation of the Fe-Zn intermetallic phases can be suppressed by adding Al to Zn, however, the resulting Fe-Al intermetallic phases can be destabilized and transform into Fe-Zn intermetallic phases when the Al content in Zn is too low.
- To prevent the Fe-Al/Fe-Zn transformation, the Al composition in the Al depleted region should be high enough, i.e., it should not cross the line A in Figure 17. CZN4AL and
CZN4ALLT results showed that 4 weight percent of Al was enough under the experimental conditions used in the study.

- To examine the phase transformation in the solid state, CZN4AL and CZN4ALLT were annealed at 300 °C for 5 days. No noticeable changes were observed at the micro-scale after the annealing. However, further studies are required to predict the long term behavior.
- Using a near eutectic Zn-Al filler allows us to do the filling process at a lower temperature. The benefits from this are twofold. First, the liquid metal corrosion rate decreases with decreasing temperature. Second, it extends the presence of the ZnO diffusion barrier during the initial stages of the filling process, which delays the growth of the Fe-Al intermetallic phases. Despite the preferential benefits of Fe-Al compared to Fe-Zn, its growth should be minimized since it also consumes Fe from the steel container.

4.2. **Recommended future work**

The following topics are recommended for future study.

- Is the expected temperature in the disposal package high enough to grow the Fe-Al intermetallic phases or to transform the preformed Fe-Al phases into Fe-Zn phases?
- What would be the safety/tolerance limit for the assembly materials, i.e., irradiated ferritic/martensitic steels, while they are in contact with liquid Zn-Al? Here, the limit refers to allowable temperature and liquid metal contact duration limit.
- Benefits of using near eutectic Zn-Al was discussed. Advantages of using hyper-eutectic Zn-Al to hypo-eutectic Zn-Al and vice versa still need to be answered.
- Having a larger volume of liquid metal causes larger volumetric shrinkage during solidification. Thus, a larger scaled experiment is essential. Here, the duct wall surrounding the fuel rods should be considered since it provides the principal discontinuity that can affect volumetric shrinkage.
- Closing the interfacial gap could have produced residual stresses. The crack formed in CZN is an evidence of this. It is known that there is a volume increase during the Fe + Al = Fe-Al reaction, which can be beneficial if we utilize it well.
• The combination of Zn coating and Zn-Al filler was used in this study mostly because of the abundant information in the literature. Consider other materials.

4.3. Answers to some encountered questions.

The author encountered several questions from colleagues and from audiences at a conference. Some questions and answers are provided here.

Q: Why do you need a container?
A: The expected temperature in the disposal package is too high for Zn-Al alloys to be used for structural purposes.

Q: Why don’t you heat the container to a high temperature, emplace the pre-made SNF containing Zn-Al (let us call it as an insert), and then cool down, so that the container can shrink and reduce the gap thickness?
A: Such an approach requires strict dimensional accuracy. The pre-made insert as well as the container should be a perfect cylinder. Any dimensional mismatch or surface roughness will still provide thermal contact resistance between the container and the insert.

Q: Why don’t you directly use a fluxing agent?
A: Appendix A gives the answer to the question. Even if an ideal flux exists, applying it to the entire inner wall of the container can be complex. Directly pouring liquid Zn-Al into a fluxed steel container was also tested but it did not work because the melt solidified too fast.
APPENDIX A:
LIMITATIONS OF DIRECT FLUXING

For metal to metal adhesion, one is readily motivated to use oxide reducing chemical agents (commonly called fluxing agents). The principle of the agents is that they decompose and produce an acid above a certain reaction threshold temperature which reduces metal oxides and produces salt residue and water. The decomposition should occur while it is in contact with metal oxides, otherwise, it will lose its functionality. As mentioned in the introduction chapter, direct use of the agents can be inappropriate for nuclear waste packages. It is not only because the reaction products are undesirable but also because preheating the container is essential, considering its dimensions and geometrical complexity, to prevent early solidification of the poured molten filler. This appendix chapter experimentally proves this argument.

Two sets of tubes and bottom lids made of low carbon steel (1005-1026 carbon steel) were prepared. 316 Stainless Steel tubes were assembled to the bottom lid to provide a pathway for a cartridge heater for future use. One of the two tubes was fluxed with the same agent, i.e., ZnCl₂/NH₄Cl (25:75 wt.%), which was used for the Zn coating in the main experiment, at 80 °C for 3 minutes and then dried at 120 °C for 3 minutes. Cylindrical blocks of pure Zn (99.6 % purity) with a center bore were prepared and inserted into the tubes. The assemblies were put inside a tray and into a box furnace for heating. Thermocouple wires were spot welded to the outer wall of the tubes. Figure 25-(a) shows the images of the components and Figure 25-(b) shows the assemblies prior to heating. The applied fluxing agent is visible on the tube wall of the assembly on the right side. The furnace was steadily heated up to 450 °C, kept at that temperature for a while, and steadily cooled down. During heating, white fume, the product of the decomposition (sublimation) of the fluxing agent, came out from the furnace. An image of the samples after heating/cooling is shown in Figure 25-(c). The residues are visible on the wall and on top of the solidified Zn of the fluxed sample. After cooling down, the samples were vertically cut into half to observe a cross sectional view. Figure 25-(d) shows the cross section of the non-fluxed sample and Figure 25-(e) shows that of the fluxed sample. Because the samples were cooled multi-directionally, the casting defect, the so-called “pipe”, was formed near the upper centerline. An interfacial gap between the container and the filler were formed in both samples and they are even visible in the images.
The effective thermal conductivity measurement process was not well-controlled; thus it is not included here.

**Figure 25.** Pictures showing (a) the tube, the Zn block, and the bottom lid used in the test, (b) the assembled components (samples) inside a box furnace, (c) samples after the test, (d) sectional view of the default sample, and (e) sectional view of the fluxed sample.
APPENDIX B:
LIMITATIONS OF Multi-DIRECTIONAL COOLING

This appendix experimentally shows the limitations of multi-directional cooling. A galvanized steel tube (purchased from a supplier) was used as the container and Zn-4wt.%Al was used as the filler. The sample was steadily heated up to 430 °C and kept at that temperature for 2 hours in a box furnace. Afterwards, the sample was taken out from the furnace and placed on top of a thermally insulating material to promote the cooling from the wall.

A cross sectional image of a cut piece of the sample is shown in Figure 26. A container-filler interfacial gap was formed. As shown in the zoomed-in optical microscope images, the Al rich phase was observed at and near the interface which means the filler was once metallically bonded to the container wall. Interestingly, the crack grew along the Al rich line close to the interface.

Figure 26. A sectional image of the sample. The zoomed-in optical microscope images show that the cracks were formed along the Al rich line.
APPENDIX C:
HEAT TRANSFER CALCULATION

This appendix shows a parametric heat transfer calculation result, a part of the work done by Nourallah Dahmen, a visiting student from the Commissariat à l'énergie atomique et aux énergies alternatives (CEA), France, at the MIT borehole group. The complete version of the work can be found in [57].

![Diagram of heat transfer calculation domain and mesh](image)

**Figure 27.** (a) The domain and (b) the mesh used in the heat transfer calculation.

The calculation assumed continuous media, consisted of fuel rods, a duct wall surrounding the fuel rods, void filler that fills the space between the rods and the duct wall and the container, a container, gap, a liner, and the granite host rock. The domain and the mesh are shown in **Figure 27**.
Volumetric heat generation from the decay heat equation for the TWR assembly was used with an assumption of a cosine cubed power profile along the axial direction, the axial-midpoint being the peak. Symmetry boundary conditions were used at the top and the bottom, and a fixed temperature condition (fixed to 80 °C) was used at the end of the host rock region. The three dimensional steady-state conduction equation was solved using the commercial finite element solver, Abaqus, by fixing everything except the thermal conductivity of the void filler. Figure 28 shows the results where the maximum temperature is plotted against the thermal conductivity of the void filler.

![Figure 28](image.png)

**Figure 28.** Maximum temperature in the emplaced disposal package as a function of the thermal conductivity of the void filler.
APPENDIX D:
EDX MAPPING OF CZN4AL AND CZN4ALLT
REFERENCES


