Étude expérimentale et numérique de la fusion contrainte d'un matériau à changement de phase (MCP) métallique

Experimental and numerical study of constrained melting of metallic phase change material (PCM)

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Résumé - La prochaine génération de réacteurs nucléaires nécessite le développement de technologies innovantes notamment dans le domaine de la sureté. L'une des technologies proposée serait constituée d'un système passif mettant à profit la chaleur latente d'un matériau à changement de phase (MCP) métallique afin d'évacuer la chaleur du réacteur en cas d'incident. Cette étude vise à identifier et caractériser les mécanismes opérants lors de la fusion de l'alliage Zamak (Zn-Al4%) à l'intérieur d'une boîte en acier inoxydable (SS430) fermée et de les modéliser afin de permettre d'établir des règles de dimensionnement. A travers différentes caractérisations à l'échelle laboratoire, nous avons pu mettre en évidence l'importance de la couche d'oxyde native sur le mouillage du MCP liquide contre l'acier inoxydable. La suite des travaux portera sur l'étude indirecte des mécanismes identifiés dans une boite en SS430 fermée via l'utilisation de l'imagerie IR.

Abstract – The demands for an improved safety for the next generation of nuclear reactors has brought the development of innovative technologies. One of this innovation is the design of a passive modular storage for the decay heat employing a metallic PCM as a heat sink. This study is focused on the experimental and numerical investigation of the melting of Zamak (Zn-Al4%) alloy inside a stainless steel (SS430) closed box. By different experimental technics, the aim is to identify and characterize the interaction mechanisms between materials to develop a numerical model to propose design rules. From lab scale experiments, we demonstrated the impact of the native oxide layer on the wetting behavior of Zamak on SS430. The next step will consist of an indirect study of the identified mechanisms in a closed SS430 box helped by IR imaging.

1. Introduction

The safety of nuclear reactors has been highlighted as a key factor to consider in the design process of the next generation of reactors [1]. This aspect has driven the research of innovative elements to fulfill the more demanding safety requirements. During the design of the loop-type ATRIUM reactor, a Sodium-cooled Fast Reactor (SFR), some innovative safety features are introduced. In order to maximize the compactness of the system a phase change material (PCM) could be used as a heat sink. The proposed solution is made of a modular heat storage unit, to

https://doi.org/10.25855/SFT2025-051

obtain a better distribution of the heat and a flexible design (see Figure 1). In this new configuration, multiple steel boxes containing the PCM are stacked one on top of the other and organized in rows around the tubes containing the thermal fluid coming from the primary vessel. In the industrial configuration, each box is quasicubic with a side length of about 60 cm and contains a block of PCM in an inert atmosphere, the heat thermal fluid (NaK) passes through the storage by a rounded shape at the corner of the insulated boxes [2]. The PCM material has to fulfill some specific requirements: high volumetric energy storage density, high thermal conductivity and melting point within the working temperatures; additionally, it must be easy to manage and be readily available. The final choice of PCM was the commercial alloy named Zamak 3 (originally from German *Zink Aluminium Magnesium Kupfer*, as some alloys contain copper), a Zinc-Aluminum alloy (4%wt Al), that presents the thermal properties in good agreement with the requirement for the application. Its compatibility with the steel selected for the unit boxes (SS430) and their interaction during working conditions have to be further analyzed.

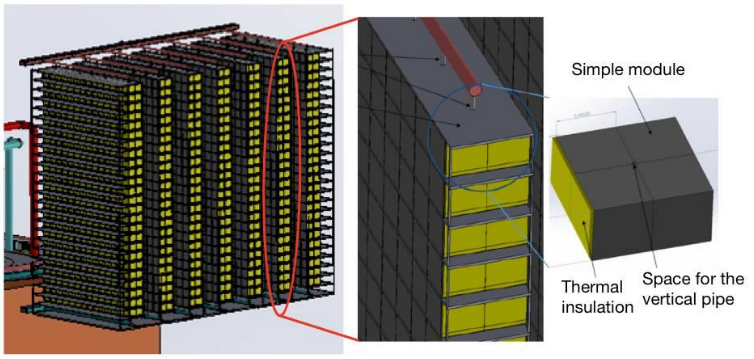


Figure 1 *: Schematic Decay Heat Removal System*

The objective of the study is to obtain a thermal model capable of describing the enclosed system. The investigation is lead at laboratory scale with the characterization of properties of the materials, their physical and chemical interactions to help to develop a thermal model based on STAR CCM+ software. The complexity and size of the industrial elementary unit calls for the simplification and downscaling of the experimental setups developed in this study. Once validated, numerical model could be applied to more complex geometries.

2. Methodology

The mechanical interactions that could occur between the materials are very complex as they should consider linear elasticity, plasticity, then viscoplasticity. For the sake of simplicity, these mechanisms will be not taken into account, thus the distance between the ingot of Zamak and the internal walls of the SS430 takes only into account the thermal expansion of the two materials. The volume between the Zamak and the internal walls of the SS430 box is filled with an inert gas.

While heating, the chemical interaction between Zamak and SS430 could produce oxidation-reduction reaction, corrosion as well as the formation of new interface materials. These reactions may modify the energy of the system (exo and endo mechanisms) as well as the molten PCM shape and its behavior on SS430, thus the thermal model. To investigate these effects, we lead two parallel studies: one dealing with the material science aspect with thermochemistry investigation helped by DSC (differential scanning calorimetry), STA (simultaneous thermal analysis), X-Ray diffraction, SEM (scanning electron microscopy) analyses and wetting characterization.

This information feeds the thermal simulation to model the thermal behavior of the system. The second study is dedicated to the validation of the model with a larger scale experiment with what we called an elementary unit box.

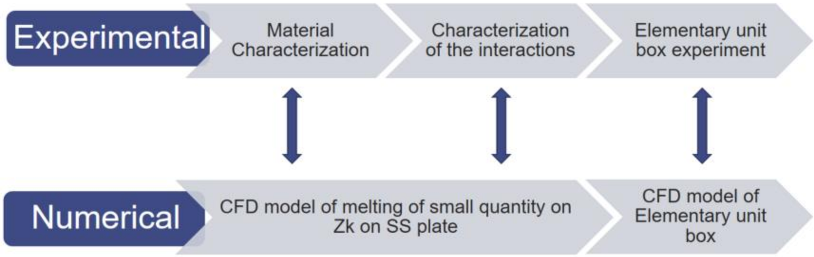


Figure 2: *Flow chart of the different steps conducted in the study*

3. Materials and experiments

3.1. Materials

Zamak (Al-Al4%wt) was provided by *Roger Fonderie-FR* in ingot shape, stainless steel 430 was provided by *Stainless Früchtl Gmbh-DE*. For the experimental parts, materials are tooled and shaped to the desired dimensions. Materials densities are 6600 kg.m^{-3} [3] and 7700 kg.m^{-3} [4] for Zamak and SS430 respectively at 20°C. The thermal conductivity taken for the study were taken to 113 W.m^{-1}.K^{-1} [3] for Zamak and 25 W.m^{-1}.K^{-1} for SS430 still at 20°C [4].

3.2. Laboratory characterization

Intrinsic properties of the materials are measured with the help of DSC (differential scanning calorimetry-C80 Kep Techologies), STA (449-F3 Jupiter Netzsch- coupled TGA and DSC), TMA (thermomechanical analysis-402 F1 Netzsch).

A laboratory experimental setup was developed to investigate the wetting behavior of Zamak on SS430. The setup consists in a tubular furnace (Nabertherm RS 120/1000/11) inside of which small samples of 10 mm edges cube of Zamak are placed on SS430 plates. The temperature inside the furnace is brought over the melting temperature at 450°C (heating rate of 7°C.min^{-1}, free cooling, under N_2) of the PCM and the spreading behavior is recorded with a camera and appropriate lighting, as shown in Figure 3. For some experiments, Zamak surface was cleaned with 37% HCl to remove its surface oxide. Similar tests on the interaction of a liquid with a solid substrate following a change of phase solid to liquid are presented in literature [5] [6] [7], they show the possibility of using real-time imaging of the melting of the sample to quantify the spreading behavior.

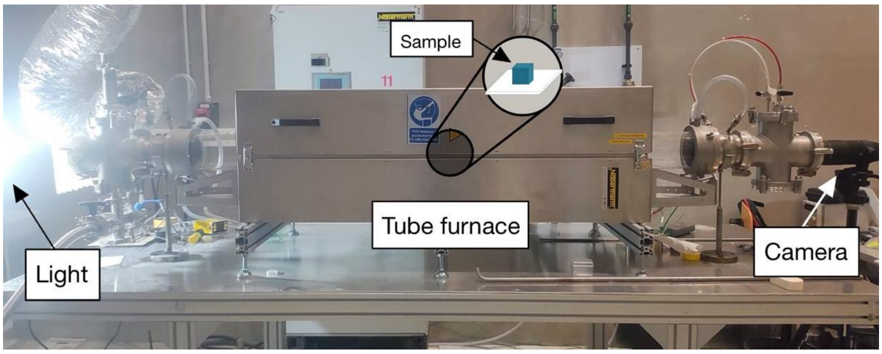


Figure 3: *Experimental setup with tube furnace*

3.3. Numerical models

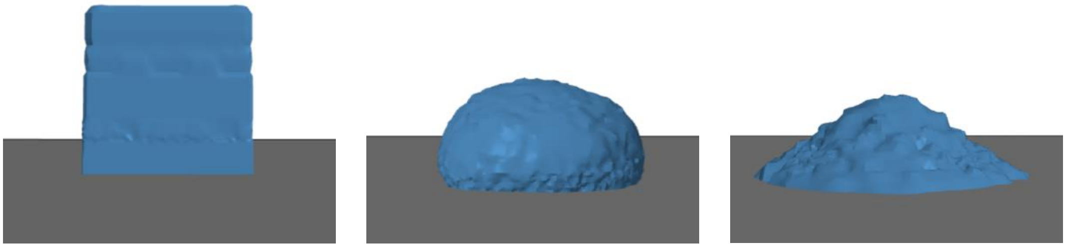
The melting-solidification modules of the commercial code STAR-CCM+ was utilized for solving the governing flow and heat transfer equations [8]. The Volume Of Fluid (VOF) multiphase method is used to reconstruct the interface between the solid and liquid phase of the PCM adopting an Eulerian fixed grid [9]. The interface is not tracked explicitly by the model, which uses an enthalpy formulation to determine the distribution of the solidified portion of the liquid-solid phase. Each mesh cell is characterized by a value of the solid volume fraction. To prevent all flows in the solid state, the optional melting-solidification flow stop model is activated; this functionality stops the flow when the value of the solid fraction in a cell is 1. This way the momentum equations are solved only in the cells that started undergoing phase change. The software requires specific parameters to define the themophysical properties of the components. The SS430 is modeled as a solid and thus is characterized by the values of density, specific heat and thermal conductivity. The Zamak, that undergoes the solid-liquid phase change, is modeled as a liquid in the multiphase module and it requires additional parameters: the solidus and liquidus temperature, the latent heat of fusion and, once melted, the dynamic viscosity. To complement the Zamak in the multiphase volume and observe an interface with the surrounding atmosphere, an ideal gas is included in the model. A phase interaction is introduced, which calls for the definition of a value for the surface tension at the liquid-gas interface and for the contact angle at the triple line, where both fluids are in contact with the wall. Similarly to what has been done by Pater *et al.* [10], the complexity of the model is added gradually.

4. Results and discussion

Thermal characterization on the materials as received shows a mean coefficient of linear thermal expansion (CLTE) of 33 10^{-6} K^{-1} and 10.2 10^{-6} K^{-1} for Zamak and SS430 respectively between 20°C and 275°C. The mean measured Cps are of 450 $J.kg^{-1}.K^{-1}$ for Zamak before melting and 490 $J.kg^{-1}.K^{-1}$ for SS430 respectively. On the TMA and DSC thermograms the solid to solid eutectoïd phase change are recorded as a change of CLTE at 277°C with an enthalpy of transformation of 6.55 $kJ.kg^{-1}$. The latent heat assimilated to the first liquid formation ($\eta+\beta \rightarrow L+\beta$) at 381°C is recorded at -148 $kJ.kg^{-1}$. All those values are in good agreement with literature values [11].

The phase change modelling capabilities of the commercial software STAR-CCM+ are first utilized to develop a model for the melting of a sample of Zamak on a stainless steel plate. To compare with the tubular furnace experiment, a cube of 10 mm edges of Zamak is modeled. An ad hoc heat flux is defined and imposed on the surface of the Zamak phase to represent the radiative heat transfer occurring inside a furnace, the value is to be further tuned to ensure it matches the heat flux that characterize the experiments. As we work using the VOF framework, the Zamak surface is not directly accessible in the software environment and the heat flux ($W.m^{-2}$) is modeled as a heat source Q ($W.m^{-3}$) and imposed in the volume cells containing the interface. The procedure is divided in two steps: a) identification of the cells containing the interface from the volume fraction field and determination of the surface area they contain; b) calculation of the heat flux, here a simple linearization of radiative heat exchange with the oven wall. Note that this method allow the simultaneous conjugate heat transfer between Zamak and inert gas.

As a first approach, the density of the PCM is kept constant and the influence of gravity is discarded. The values of the properties of the Zamak and the SS430 required by the model, as presented in section 3.3 are taken from literature and reported in Table 1. The value for the contact angle, that describes the spreading behavior of the molten Zamak, is one of the representative parameters of interest for the materials interaction. The effect of the modification of the value of this parameter is shown in Figure 4.



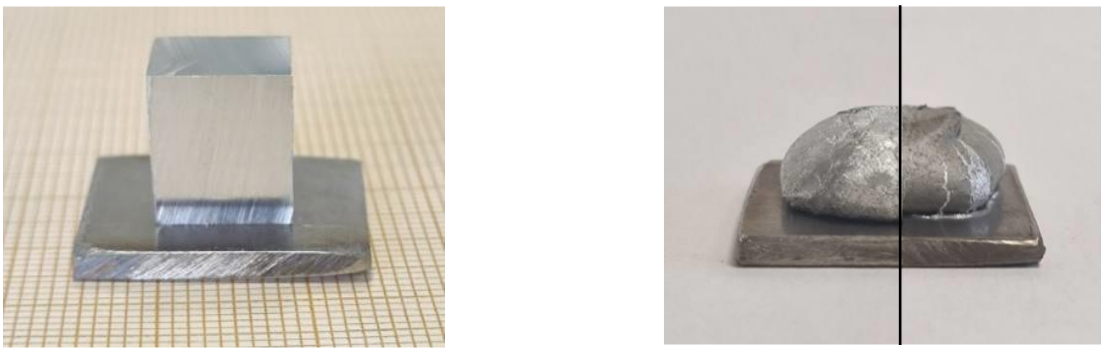
(a) (b) (c)

Figure 4: *STAR-CCM+ simulation of PCM melting with different contact angles: (a) initial state, (b) Contact angle: 120°, (c) contact angle: 40°*

	ρ	c_p	κ	T_s-T_l	H_f	μ*	γ*
	$kg.m^{-3}$	$J.kg^{-1}.K^{-1}$	$W.m^{-1}.K^{-1}$	°C	$kJ.kg^{-1}$	Pa.s	$N.m^{-1}$
Zamak	6600	419	113	381-387	110	$2.65.10^{-3}$	0.758
SS430	7700	460	25	-	-	-	-

Table 1: *Properties of Zamak* [11] *and SS430* [4] *@20°C. *Value taken for Zinc* [12]

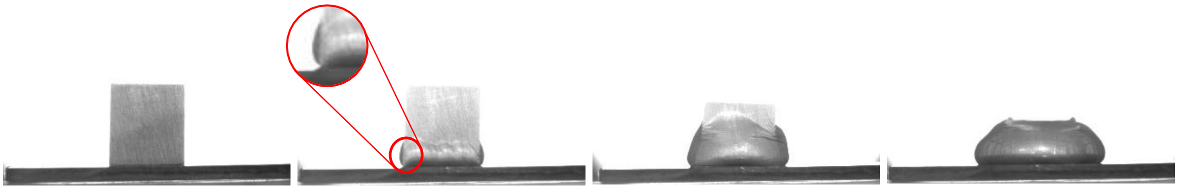
Figure 5 shows the experimental results of the melting, when Zamak is not cleaned with HCl, the molten Zamak, once solidified demonstrates no adhesion on the stainless steel plate and the original shape of the sample is still partially recognizable. This phenomenon is attributed to the native oxide layer that forms on the surface of the Zinc-Aluminum alloy when exposed to oxidative atmospheric conditions [13]. This layer acts as an outer shell during the melting process and later as a diffusion barrier preventing from liquid to solid chemical interactions. When the shell dynamically breaks or is chemically removed (see Figure 5), the evolution of the interaction is vastly different. The molten PCM spreads on the SS430 plate with high chemical adhesion.



(a) (b)

Figure 5: *Experimental results for melting of Zamak on SS plate. (a) Zamak on SS430 before heating, (b) after eat treatment at 450°C, left half without surface HCl cleaning, right half with HCl surface cleaning*

The influence of this surface layer on the dynamics of phase change can be observed in the sequence of images reported in Figure 6 and Figure 7, where the melting process inside the furnace for, respectively, raw Zamak and Zamak with a chemically-treated surface is recorded. For the former specimen, it is clearly visible the deformation of the outer layer to allow the displacement of the molten alloy inside. As highlighted in image b of both sequences, at the onset of melting, the molten metal on the inside concentrates at the bottom of the samples, creating a visible protrusion. The evolution of the surface behavior then changes for the two cases. When the surface of Zamak is chemically treated to remove the oxide layer (Figure 7), the edges are subjected to opening due to stress concentration (see images c and d). Whereas, for raw Zamak the corner deforms, as emphasized by the presence of creasing, and homogeneous fissuring is observable on the surface. This two experiments show the influence that the characteristics of the surface have on the dynamics of melting.



(a) Room temperature (b) Melting temperature (c) Above melting T (d) At 450°C

Figure 6: *Melting of raw Zamak on SS, front view. Sequence of images*

(a) Room temperature (b) Melting temperature (c) Above melting T (d) At 450°C

Figure 7: *Melting of Zamak cleaned with HCl, angled view. Sequence of images*

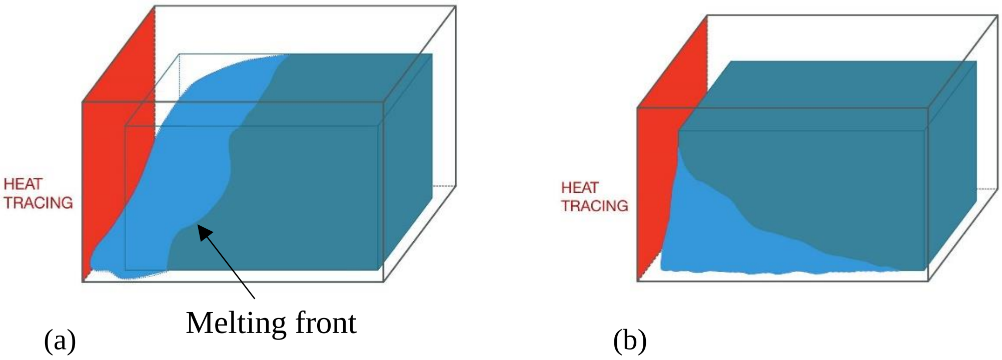
Additionally, these experiments highlight both the affinity of the materials and the possible drastic change in behavior with the upscale of the size of Zamak. By upscaling to the size of the Zabox setup, the surface to volume ratio decreases by 94%, the internal pressure of the liquid on the surface oxide layer may lead to its failure and trigger chemical interactions. Therefore, it is foreseeable that the affinity observed in the test where the surface of Zamak is chemically treated is more representative of the interactions that would characterize the tests in the Zabox setup. The oxide crust on the surface of Zamak, with the same thickness and mechanical properties than the one present at the small scale, will have to withstand an increase of the internal pressure due to the increase in size. The break of the crust will result in the direct interaction of the molten bulk with the material of the plate. At the time of writing, a contact angle of 120° seems to be representative of the melting behavior of Zamak even it doesn't consider the adhesive aspect. Indeed, the consequences of this crust breaking on the industrial thermal model are not easy to predict and require more experiment investigations for the model development.

5. Conclusions and Prospective

Laboratory experiments and numerical methodology employed for the study have been presented, as well as the preliminary results obtained.

According to the PCM chemical surface, the interactions and spreading of PCM on the SS430 change. The numerical model will have to consider this aspect to simulate a closed box as the experimental results introduce an expected non-linearity. It seems that the outside PCM layer may acts as a diffusion barrier and influence the thermomechanical as well as the chemical behavior of the system at larger scale, which would modify the thermal model. Therefore, the tuning of the parameters of the simulation with experimental feedback is necessary to accurately describe the evolution of the thermophysical behavior of an industrial representative closed box.

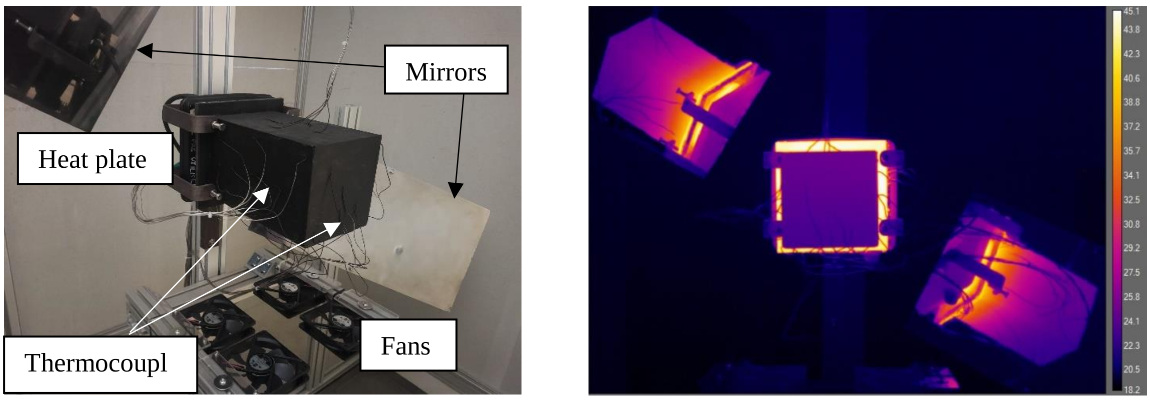
The problem of constrained melting of a metallic PCM inside an opaque stainless steel box requires the development of an experimental bench described hereafter. It will provide additional information on the behavior of the system at a larger scale and will later allow for the validation of the corresponding model. For better understanding, two possible scenarios of the melting of Zamak in the SS430 closed box are depicted in Figure 8, which underline the importance of an experimental campaign for the model development.



(a) (b)

Figure 8: *Schematic of possible melting scenario of the experimental box (a) melting by heating side (b) melting by the bottom*

The experimental setup named “ZABOX” being characterized for operation consists in a simplified geometry of the industrial design (15x15x25 cm). The box is heated on one side with an electrical heater and an air flux is imposed on the outer walls with fans in order to allow the quantification of forced convection. The temperature of the outer surface of the box in mapped using type K thermocouples and infrared imaging (FLIR 655sc 25°) thanks to two aluminum mirrors (see Figure 9). Once the objective of the study of confirming the model’s ability to simulate the proposed closed box is reached, the resulting model could be applied to more complex geometries closer to ones of the industrial design.



(a) (b)

Figure 9: *Experimental box ZABOX setup under characterization (a) picture of the setup up close, (b) IR image of the front side and the IR reflection on the mirror*

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