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# Cast Structures Improving Thermal Conductivity for Energy Storage

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## Abstract

Thermal energy encounters a huge demand in the world, part of which can be met by renewable energy sources, such as solar energy, and storage of thermal energy surplus from industrial processes. For this purpose, thermal energy storage (TES) units, in which heat is stored, are developed. The energy is accumulated by phase change materials (PCM) characterized by high phase transition enthalpy. PCMs have poor thermal conductivity; therefore, to take full advantage of their capabilities and to accelerate the charging and discharging cycle, metallic structures are used. These structures are manufactured using investment casting technology. Creating models with additive methods, such as 3D printing, allows obtaining complex shapes with high accuracy, such as thin-walled castings. At a large scale, the method may not be cost-effective. In this paper, the heat exchanger models were made from PLA and the castings - from AC44200 aluminum alloy. Investment casting requires the proper selection of parameters, such as the right material for the model, the selection of the firing temperature, the adjustment of the temperature of the molten metal, the temperature of the mold, and the pressure in it. Misaligning any of the parameters can lead to imperfections on the finished casting. Based on the model roughness study, it was found that minor roughness and higher accuracy are presented by the lower parts of the casting, while weaker performance is observed for the upper parts. Metal castings in a salt PCM environment may be subjected to corrosion. Therefore, the authors proposed to produce protective coatings on aluminum castings by the PEO method - plasma electrolytic oxidation. Porous ceramic thin films consisting mainly of alumina were obtained. The next tests will be aimed to confirm whether this layer will not negatively influence the thermal conductivity of the thermal energy storage.

**Keywords:** Environment protection, Product development, Investment casting, Energy storage, Heat enhancer

## 1. Introduction

According to “Renewables 2019 Analysis and forecast to 2024” by International Energy Agency, heat is the largest energy end-use, as it accounts for about half of total energy consumption in 2018, and 50% of that was used in the industrial processes. Mainly fossil fuels are predominant among the heat sources in the world, however, the consumption of renewable heat is forecast to increase from 10% in 2018 to 12% by 2024 [1]. It does not seem to allow us to get significantly closer to international targets for

preventing climate change, but from a consumer and business perspective, an increase in renewable energy use and storage is to be expected. A method to reduce heat loss in industrial processes should be determined. Storage of such surpluses can be a solution.

Among many renewable energy sources, solar power appears to be a valuable source of heat energy. The solar heat for industrial processes market expands, significant growth in solar thermal energy is expected in the Middle East, North Africa, India, and South American countries, while the US, China, and



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the European Union are already experiencing growth in the use of solar thermal energy [1].

PCMs (Phase Change Materials), being an example of Latent Heat Storage (LHS), accumulate heat energy during phase change processes while heating in particular temperatures (e.g. melting or evaporating temperatures). The energy can be released by cooling down the material (solidification of melted PCM) [2]. A wide range of different materials can be used as PCM, depending on their properties, such as phase change enthalpy, lifetime, degradability, the phase transition temperature, price, or thermal conductivity. That is why the phase change materials are usually divided as presented in Figure 1.

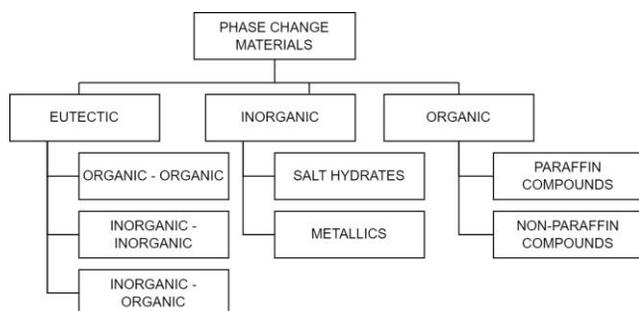


Fig. 1. Classification of PCM by material type [3]

Since PCMs often feature low thermal conductivity, charging and discharging (melting and colling) of high volume deposits may be time-consuming. That is why metal heat enhancers were proposed. Various shapes of enhancers have been studied and reported in the literature. In [4] authors present a pin-fin structure as an enhancer. The tests of charging and discharging were run in the paraffin wax deposit and confirmed the improvement of the charging rate by the use of the enhancer. Similar tests were conducted for honeycomb spatial structures. The authors investigated whether vertically or horizontally placed elements will improve the charging cycle better, and concluded that apart from thermal conduction, the convection was improved by the horizontal location of the enhancer as well [5]. Moreover, foam-like structures were tested as a potential enhancer for PCM deposits. In the case of metal foam – paraffin PCM system, the PPI (pores per inch number) can play a significant role due to the natural convection changes. Tao et al. proved that the porosity and natural convection are dependent, thus each change of the parameters can significantly influence the performance of TES [6]. Similarly, the test of metal foam-infused PCMs was conducted in [7]. Different fill height ratios and metal foam porosities were tested and compared. The experiment concludes that depending on whether the main objective is the economy and capacity of the TES or the melting rate of the deposit, a high or low foam porosity should be chosen, respectively. This is related to the fact that high porosity foams are cheaper, but full melting of the deposit will be more difficult than in the case of low porosity foams, which are more expensive materials. An additional approach to enhance relatively low heat transfer properties of PCM materials might be to apply various fillers within them (graphite fiber preforms, porous matrices, nanofillers (MXenes, graphite, Cu, graphene, carbon nanotubes (CNTs)), silica or alumina catalysts, which were described in [8–10]). For

metal cast spatial structures, investment casting appears to be an effective method of production.

Investment casting is a commonly known foundry method, used especially in the production of art, weapons, or jewellery. It is still one of the most popular methods used by sculptors and artists due to its high accuracy of model reproduction and very good surface finish of the cast part, as well as among engineers in charge of design and manufacturing of components like turbocharger wheels, pick-holders, etc. [11]. The popularity of this method is also related to the possibility of rapid prototyping and relatively low costs of production, especially in rapid tooling, where easy customization of obtained products is high priority [12]. It is possible to produce models with different types of additive methods such as stereolithography (SL), selective laser sintering (SLS), laminated object manufacturing (LOM), and fused deposition modeling (FDM). Nevertheless, one has to remember that the use of described methods is a relatively new technology, that is why each user should adapt the process to their materials and requirements by choosing a proper model manufacturing method and materials [13].

3D printing technology using plastic or filament (FFF – fused filament fabrication, or FDM) is an additive technology increasingly used in various industries using investment casting for production. In the article [14] the researchers designed, modeled, and printed elements for orthodontic applications, which were then cast and finished. After postprocessing, the elements were comparable to the parts prepared traditionally. Additive manufacturing is also an appreciated method of model production for parts with extremely thin walls, e.g. approx. 0.4 mm. However, it has been proven that the choice of printing material will directly affect the quality of the completed part. Körber et al. [15] tested several different polymers for thin-walled nickel-based superalloy casts. They found out that not all materials were able to burn out properly, without cracking of the shell mold. This is an aspect that for each alloy and polymer should be tested and adjusted.

Nevertheless, the aggressive nature of the solar salts – the most popular and commonly used PCMs, may cause corrosion of the metal elements placed in the system, both the container and the enhancers [2]. That is why plasma electrolytic oxidation (PEO) coatings are proposed to protect the metal inserts. PEO is used typically for lightweight metals, such as aluminum or magnesium. The coating process is held in low-concentration alkaline electrolyte, based on ex.  $\text{Na}_2\text{SiO}_3$ ,  $\text{NaOH}$ ,  $\text{KOH}$  [16]. As the product of the reaction, the thin ceramic porous layer can be obtained on the metal sample which should significantly prolong the lifetime of the TES unit. Depending on the temperature, the concentration of the electrolyte, voltage and time of the process duration, different layers characterized by different crystalline structures, porosity, roughness, or chemical composition are obtained [17].

It is worth noting that ceramic oxide layers may cause a slight decrease in the thermal conductivity of the heat transfer enhancers, which may be a significant drawback of such a solution of the corrosivity problem. Nevertheless, it was also pointed in the literature, that there is a possibility to improve the thermal conductivity of layers coated with PEO. In the paper [18], the addition of carbon nanotubes into the electrolyte decreased the number of micropores and cracks on the oxide layer, increasing

thermal conductivity at the same time. Thanks to its structure, graphene builds well into the porosity of the oxide layer, so its presence improves the anti-corrosion properties [19, 20].

In the following paper, the authors will try to present the method of manufacturing heat exchangers by investment casting. They will also point out the most frequent problems and mistakes encountered in the technology and present applications in the thermal energy field and methods to prevent the rapid deterioration of castings.

## 2. Materials and methods

Metal inserts were prepared in the means of investment casting. The method of the preparation was similar to the one described in [5]. Firstly, the spatial structures were modeled in Autodesk Inventor Professional program. G-code files were prepared with the use of Simplify 3D and Prusa Slicer programs. Spatial structures were printed on HBOT F300 and Prusa i3MK3 printers. The PLA (polylactide) with different color pigmentation was used. The layer height was set to 0.2 mm, and the nozzle diameter varied from 0.4 to 0.6 mm depending on the sample. Such prepared elements were molded with plaster and burned out at a temperature of about 720°C. A vacuum was created in the hot mold and the molten aluminum alloy was cast in it. The alloy used in the process was AC 44200. Chemical composition can be seen in Table 1. Figure 2 presents a flow chart of the investment casting process. The specimen dimensions were 200 mm in height and 106 mm in diameter.

Table 1.  
Composition of AC 44200 alloy

Element	Si	Fe	Cu	Mn	Zn	Ti
%	10.5 – 13.5	0.55	0.05	0.35	0.10	0.15

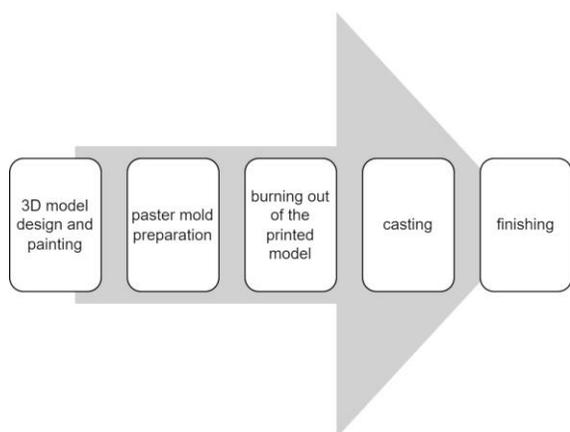


Fig. 2. Flow chart of the investment casting

Small specimens were cut off the cast enhancers and the PEO treatment was carried out in the custom-made apparatus. The electrolyte composition and concentration are placed in Table 2. The process was carried out for 300 s and the voltage applied was 600 V. After the process, the samples were dipped in distilled water and dried up.

Table 2.

The composition of electrolytes used during the PEO process for AC 44200 samples

Substance	KOH	Na <sub>2</sub> SiO <sub>3</sub>
Concentration (g/l)	10	10

To confirm quality and determine the composition of obtained elements, roughness tests were carried out with the Mehr Surf PS 10 profilometer. The surface roughness parameters (Ra – arithmetical mean roughness; Rz – mean roughness depth) of the cast element were measured. The tests were taken in the top part of the enhancer's wall (h: 180-184 mm) and the bottom part (h: 20-24 mm), and repeated 6 times. The sample used for the test was 200 mm long.

The microscopic observations of the surface before and after PEO coating were performed using the Hitachi TM-3000 Scanning Electron Microscope. The EDS tests were executed to confirm the formation of metal oxides on the sample surface as well.

## 3. Results discussion

### 3.1. Defects observed after casting

During the casting of such complex shapes, many obstacles and difficulties can be encountered. Therefore, it is crucial to choose the right parameters of the process, beginning with the materials to be used for models, to the technical parameters of the act of casting – low pressure, preheated mold. One of the most integral aspects of parameters selection seems to be the right filament choice. The result of the contamination remaining in the mold after burning out the plastic model can be seen (see Figure 3a, b). The plastic used for the model printing might have had an additional filler or pigment with good resistance to high temperature. The model did not burn out completely and the residues were floated to the upper parts of the mold while casting with molten metal. Figure 3c emphasizes the importance of the filament type as well, where the exchanger model was prepared with two different materials. The plain part was printed out of a red filament, while the part with cavities and shrinkage moles was modeled with a grey filament containing glitter. A low temperature of molten metal during pouring and unsuitable pressure might have a high impact on filling the form (Fig. 3d). Similar observations about the defects depicted below were presented in [21]. A correctly made casting is visible in Figure 4.

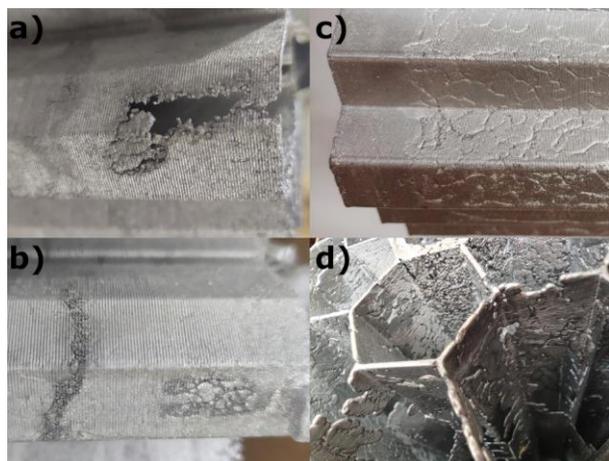


Fig. 3. Exemplary defects observed on the cast elements: a, b) contaminations due to incomplete burn out of the model; c) change of the structure of the cast due to the use of two materials with different burn out temperatures and compositions; d) shrinkage of the casting metal caused by solidification before filling the form

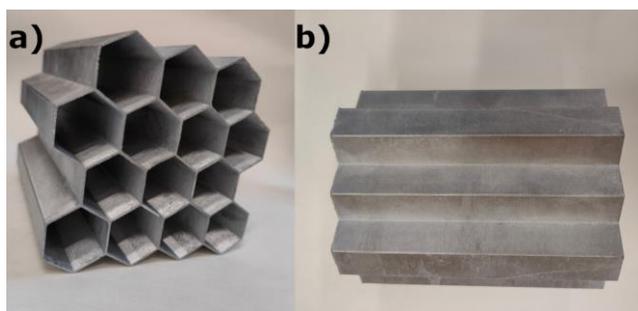


Fig. 4. Properly cast element: a) upfront; b) from the side

### 3.2. Roughness analysis

Table 3 presents average profile parameters Ra and Rz for the top and bottom parts of the enhancer's wall. The roughness profiles of the top and bottom parts of the enhancer differ noticeably, although this does not affect the performance of the finished element (see Figure 5). The variations are related to the fact that during the casting of a component, the bottom of the mold is initially filled by gravity. Then, as the mold is filled with metal, any potentially present impurities are lifted upward with the rising surface of the metal. The contaminations are burned out in the high temperature of molten metal, however, metal does not obtain a perfect reflection of the form during cooling and setting, thus higher roughness is visible.

For polymer model, the parameters Ra and Rz are similar in value to the cast structure. As can be seen in Figure 5, the linear roughness profiles for top and bottom parts of the pattern are more comparable than in the case of a cast structure, which is related to the contamination presence mentioned before. Nevertheless, the differences obtained between the model and cast

surfaces are marginal. Investment casting method allowed achieving a casting reproducing model accurately.

Table 3.

Surface roughness parameters Ra and Rz with calculated standard deviation  $\sigma$  for cast structure and polymer model

	M	$\sigma$
Cast structure:		
top		
Ra ( $\mu\text{m}$ )	21.96	0.48
Rz ( $\mu\text{m}$ )	96.48	4.66
bottom		
Ra ( $\mu\text{m}$ )	20.20	0.40
Rz ( $\mu\text{m}$ )	85.00	3.48
Polymer model:		
top		
Ra ( $\mu\text{m}$ )	21.89	0.46
Rz ( $\mu\text{m}$ )	91.27	1.53
bottom		
Ra ( $\mu\text{m}$ )	20.85	0.56
Rz ( $\mu\text{m}$ )	88.58	1.06

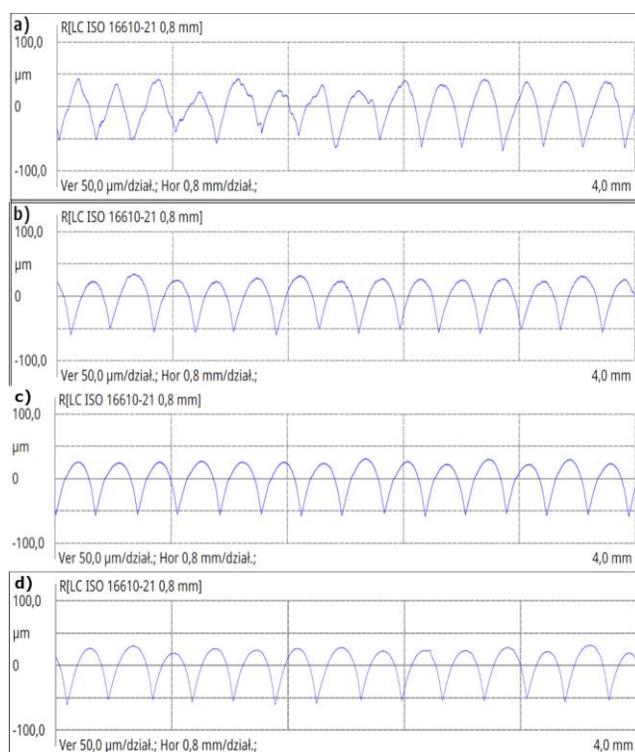


Fig. 5. Surface linear roughness profiles for: a) the top part of the cast enhancer (h: 180-184 mm); b) the bottom part of the cast enhancer (h: 20-24 mm); c) the top part of the polymer model (h: 180-184 mm); d) the bottom part of the polymer model

### 3.3. SEM and EDS analysis

The results of the EDS analysis can be seen in Table 4 and Figure 6. The appearance of a significant amount of oxygen content in the composition confirms the establishment of new compounds on the metal plate surface. In addition, the slight presence of potassium and silicon indicates the composition of electrolyte solution used during the formation of the oxide layer.

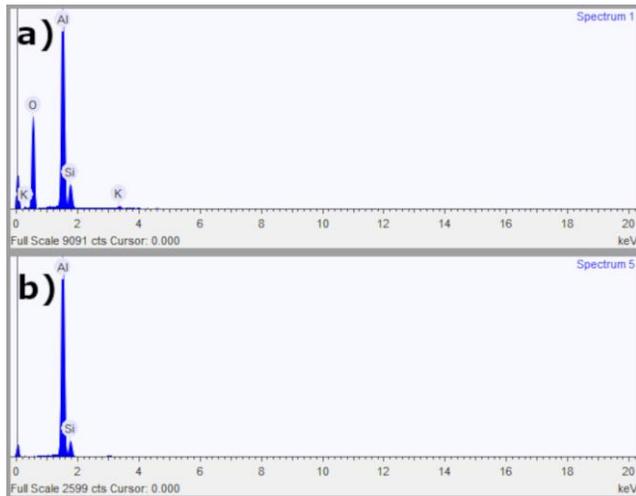


Fig. 6. EDS results were obtained for a) Aluminum alloy cast sample covered with PEO in an electrolyte solution with KOH and Na<sub>2</sub>SiO<sub>3</sub>, b) cleaned aluminum alloy cast sample

Table 4.

The atomic composition of the measured samples received in EDS analysis

Element	Atomic %	
	PEO	as cast
Oxygen	66.981	83.811
Aluminum	27.570	16.189
Silicon	5.040	-
Potassium	0.410	-

As can be seen in Figure 7a, the oxide layer is characterized by high porosity. The obtained pores' diameters are a few micrometers in size. PEO forms a coating on a sample surface, which contains two or three layers, depending on the process parameters – the inner ones are more dense, compact oxide layers, while the outer layer is characterized by open porosity formed during plasma discharges throughout the process. Firstly, the high voltage causes the creation of discharge channels and melting or diffusion of alloy elements. Then, the discharge channels are cooled down by the electrolyte and the melted substances solidify, while the gases produced start to escape from the channels. Solidified material thickens the coating, and the gas escaping indicates the porous structures [22]. The cracked surface draws attention to the brittleness of the resulting material - the damage occurred during samples cutting and preparation. Figure 7b shows

the surface of the casting before PEO coating, bright spots are visible suggesting the presence of Si in the alloy composition. The differences between the coated and uncoated insert surfaces are due to the formation of a uniform oxide layer (Figure 7c), which partially filled the casting cavities (visible on Figure 7d – uncoated sample) created by the model fabrication technology (FDM print layer).

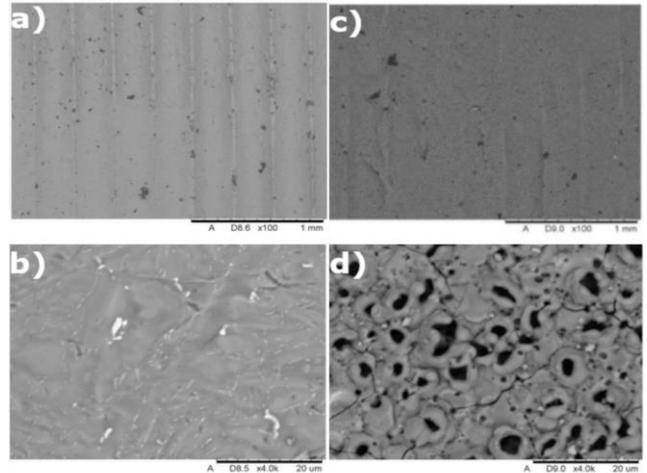


Fig. 7. The surface of the cast samples before (a,b) and after coating with PEO (c,d)

## 4. Conclusions

The exemplary cast heat enhancers were produced via investment casting, and covered with anticorrosive layer by the means of plasma electrolytic oxidation. The following conclusions were drawn:

- The use of 3D programs to design and additive methods to manufacture models, then casting with investment casting technology allows obtaining elements with high accuracy and quality of the surface.
- The difference between surfaces' roughness is connected to the way the castings were made. Parts filled with metal at the beginning of the process achieved a more precise surface, while those cast at the end – a negligible weaker finish of the surface. The problem can be neglected in the proposed application – enhancement of heat flow in thermal energy storage.
- Samples taken from the castings were subjected to PEO to develop an anti-corrosion coating. The produced ceramic coatings were composed mainly of aluminum oxides and silicon, i.e. the substances forming the casting alloy. Additionally, the presence of potassium from the electrolyte solution was observed. The coatings were characterized by high porosity.

The examination of the corrosion behavior and durability of the coated enhancers will be carried out as a next step of the research.

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