

ORIGINAL ARTICLE



Ultra-high performance alkali-activated slag as a reusable mold for light metal casting

Janna Link¹ | Alexander Wetzel¹ | Sebastian Müller² | Bernhard Middendorf¹

Correspondence

Janna Link
University of Kassel
Inst. for Structural Engineering
Department of Structural Materials and Construction Chemistry
Mönchebergstraße 7
34125 Kassel
Email: janna.link@uni-kassel.de

¹ Kassel University, Kassel, Germany

² Friedrich-Alexander-Universität, Erlangen-Nürnberg, Germany

Abstract

Light metal die casting is usually performed using steel molds. However, these lead to a reduced quality of the casting due to the occurrence of metal corrosion on the surface and the incorporation of hydrogen into the casting as a result of required process chemistry. Ultra-high performance concrete based on alkali-activated slag can be used to produce mineral molds for aluminum casting. The use of reusable mineral molds not only enables the production of various thin-walled geometries. The risk of metal corrosion is eliminated and the concrete molds can withstand multiple cycles due to their thermal stability and high strength, making them potentially superior to the already common lost mineral molds.

Keywords

Aluminum casting, alkali-activated materials, ultra-high performance concrete, thermal resistance

1 Introduction

Light metal casting and especially aluminum casting have gained in importance in recent years. The automotive and aerospace industries, but also civil engineering, require weight savings due to high transport costs and demands on emission retrenchments. In the building sector, lightweight components are necessary to keep the loads as low as possible, for example in aluminum exterior wall cladding.

The production of aluminum components based on die casting is divided into two main casting processes. A distinction is made between a gravity-driven casting (permanent mold casting), in which the molten aluminum is poured into a mold and, if necessary, solidifies under only slight pressurization. In addition to permanent mold casting, the die casting process [1] exists, in which pressures of up to 1000 bar are used to fill the mold. In both processes, the atmosphere is partly reduced during mold filling in order to achieve better component properties.

These dies are usually made of steel. Due to the high thermal conductivity of the steel molds and the associated high solidification rate of the aluminum melt, the microstructure is very fine, but when producing thin-walled geometries a certain amount of pressure is needed to fill the steel mold quickly before the melt solidifies at an early stage. another problem area is the formation of porosities, which are mainly caused by the introduction of hydrogen into the melt. To avoid that the aluminum melt sticks to the steel mold the dies are pretreated and sprayed with a release

agent, pressed together and then filled with the desired aluminum alloy (with or without the aid of additional pressure). This process is easy to automate and is therefore a standard process for the manufacturing of automotive parts etc. However, the use of steel dies has some disadvantages: The mold spraying which is necessary to ensure an optimal demolding of the cast components, is usually done by water-based demolding agents. The casting process is carried out under high temperatures above 600 °C and the water-containing agents vaporize immediately. As the aluminum melt solidifies, the solubility of gases, especially hydrogen also decreases [2].

Water from the demolding agent combines with the reactive aluminum melt to form aluminum oxide, leaving elemental hydrogen which remains as a cluster in the cast.

Hydrogen forms gas pores in the cast which leads to deterioration in mechanical properties, fatigue and shortened durability [1, 2]. For this reason, either the melt must be purified for example with ceramic foam filters [3], so that there are fewer impurities and thus fewer nuclei in it, where gas pores can form. Another option is to carry out quality-assuring non-destructive workpiece inspections at the end of the production process. Castings with high porosity have to be rejected which leads to higher scrap rates and consequently increasing production costs.

In addition to this, the use of steel molds in combination with aluminum melt leads to metal corrosion, which in turn has a negative impact on the surface quality of the cast component [4].

A mineral high-strength and temperature-resistant material would be more suitable as a reusable mold for aluminum castings than a lost mold. These properties can be met by ultra-high performance concrete (UHPC) with regard to the special requirements of the casting process.

The high compressive strength of 150–200 N/mm² that characterizes UHPC is achieved, among other methods, by packing density optimization and a low water to binder ratio (w/b) [5]. The thermal resistance of the material is increased by the addition of regenerated cellulose fibers (RC fibers). RC fibers decompose at elevated temperatures and form cavities, resulting in increased permeability of the material. At high temperatures over 100°C, physically and chemically bound water is released. The resulting water vapor pressure can be reduced by the increased permeability, resulting in increased temperature resistance for the mineral-bonded material [6].

Usually, UHPC is manufactured by using ordinary Portland cement – but ultra-high performance materials can also be based on alkali-activated materials (AAM) [7]. AAM are composed of aluminosilicic solids and as the solid precursors are less hydraulic than ordinary Portland cement they depend on activation by an alkali-hydroxide, -waterglass or -carbonate to develop strength. The solid precursors need to contain Si and Al – often secondary raw materials from industrial processes such as granulated blast furnace slag or fly ash are used. Other reactive precursors can feature silica fume and metakaolin [8].

Depending on the chemical composition of the starting products – especially the calcium content of the precursors – amorphous to nanocrystalline spatial networks are formed, which form a dense microstructure and contribute to the strength and durability of the AAM. Alkalis from the activator solution and the aluminosilicic solids form N-A-S-(H) phases, where the "N" stands for alkalis. In the case of calcium-containing solid sources such as granulated blast furnace slag, so-called C-A-S-H phases are also formed [9]. In contrast to C-S-H phases in Portland cement-based systems, these C-A-S-H and N-A-S-H phases are much more thermally stable [10] as these reaction products of AAM contain less to no chemically bound water. Challenges in the use of AAM are, on the one hand, the high shrinkage [11]. On the other hand, the rheological properties and water demand cannot be optimized by superplasticizers as in the case of Portland-cement based UHPC because conventional superplasticizers are unstable in the highly alkaline environment of AAMs. By using silica fume, the workability of AAM can be improved and low water/binder ratios can be achieved, resulting in high strength [7, 12]. Since the compressive strength of these high-performance AAM is similar to that of UHPC, these materials can be referred to as AAM-UHPC. Due to the higher percentage of chemically bound water in OPC-UHPC, the dense matrix and the degradation of the strength-bearing C-S-H-phases at elevated temperatures, AAM-UHPC are favored for use as casting die material. The positive effect on the thermal stability of UHPC due to the use of regenerated cellulose fibers was combined here with the more thermally stable AAM as a binder.

2 Materials and methods

2.1 AAM-UHPC formulation

The special application as a die entails various requirements: AAM-UHPC must remain resistant under extreme temperature loads (molten aluminum usually holds a temperature of over 700°C). Despite high stresses no spontaneous failure must occur.

The AAM-UHPC formulation shown in Table 1 is based on previous studies [12]. RC-fibers at a percentage of 0.4 Vol.-% have been added to optimize thermal stability. Solid precursors were granulated ground blast furnace slag and silica fume. Quartz sand was used as aggregate for the fraction of 0 to 0.5 mm and quartz flour as a fine aggregate and filler. In relation to the binder content 1.0 Vol.-% of mass hydrophobizing agent was added to increase the wettability of the fresh material and thus achieve a low-defect surface. Potassium waterglass with a solid content of 53 % and a modulus of 1 (molar ratio SiO₂:K₂O) was used as activator.

Table 1 Masses of AAM-UHPC components for mixing volume of 1 liter

Component	Weight [kg]
Potassium waterglass	0.3977
Granulated ground blast furnace slag	0.5319
Silica fume	0.2953
Hydrophobic agent	0.0083
Quartz powder	0.1576
Quartz sand	0.9848
RC-fibers	0.0030

In previous investigations this mixture was able to achieve high compressive strengths with sufficient workability at the same time without the use of superplasticizer. With the compressive strength of 194 MPa after 28 days the mixture can be classified in the ultra-high performance range and will be referred to as AAM-UHPC. Despite the low w/b-ratio of 0.23 the sufficient workability is ensured by the addition of silica fume. It was shown that this has a positive effect on the flowability of alkali-activated materials. [7].

2.2 Manufacture of the dies and casting experiments

The manufacturing process described below was used to produce dies (Fig. 2). The dies were used for casting of aluminum over several cycles to test the multiple use of the dies. Additionally, cubes with an edge length of 5 cm were produced for compressive strength tests. The specimens were subjected to shock temperature loading (further explained in 2.3) and the compressive strength after extreme thermal loading was compared to the compressive strength without any thermal load. In addition, the porosity of the material after this extreme temperature loading

was investigated and thermogravimetric analyses were performed.

The mold in which the AAM-UHPC is poured in to generate the dies was milled from polytetrafluorethylene (PTFE) and can be used several times. PTFE is an excellent material for creating a smooth mold surface because it has a very low coefficient of friction, low surface tension and is resistant to the highly alkaline environment of the fresh AAM-UHPC. Plastic sidewalls were mounted around the PTFE base plate with the casting geometry (Fig. 1).

The mixing was carried out with a 1L intensive mixer from Eirich. First, the dry components were homogenized for 60 s except for the sand. Then, during mixing, the potassium water glass was added and mixed for another 60 seconds. This was followed by an intensive mixing phase in which mixing was carried out at double speed for 60 s, after which there was a mixing pause to remove any residues or dry materials from the edge of the container. When the mixer was restarted (now again at normal speed), the sand was added, followed by the RC fibers. The RC fibers were soaked with a mixture of water glass and the hydrophobizing agent for better dispersion of the fibers in the fresh binder. After a total mixing time of 8 min, the prepared PTFE mold was first half filled and vibrated at 50 Hz for 2 min to allow all enclosed air to escape. Then the remaining half was poured into the PTFE molds and again vibrated for 2 min. Without covering the molds, they remained at standard climate (20°C, 65 % rel. humidity) for one day before they were demolded.

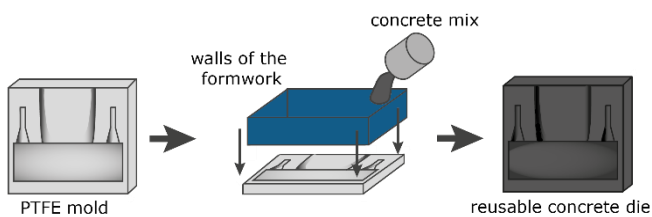


Figure 1 Manufacturing process of the AAM-UHPC dies

The cube samples remained for compressive strength testing and temperature stress testing and were stored at norm climate for a total of 7 days. On the 7th day followed the compressive strength test and before that the temperature load test. The shock temperature load tests are explained further in 2.3. After the specimens had cooled down in air, they were also tested for compressive strength.

The dies were stored for at least 2 weeks at standard climate and then delivered to the Chair of Casting Technology in Fürth where they were used for casting of aluminum alloy (Fig. 2).

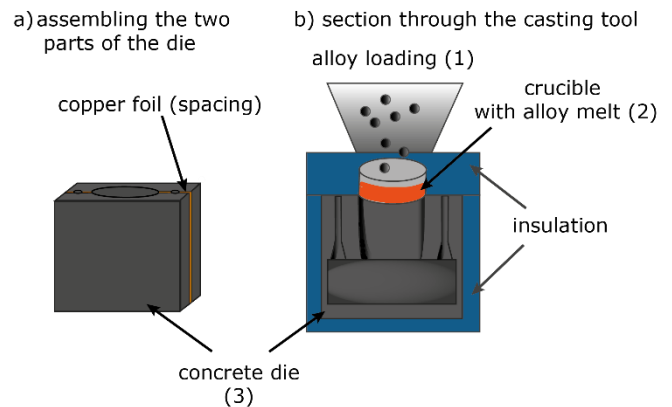


Figure 2 Casting process with the AAM-UHPC dies

Casting was carried out with an Indutherm VC 650 V unit under a casting pressure of 3 bar.

First, the dies were preheated to 300°C with a heating rate of 600°C/hour. During preheating physically bond and in parts chemically bond water leaks out of the die. Moreover, the preheating reduces the mechanical load on the die due to the thermal shock. During the preheating of the dies, the casting machine is charged with aluminum (1), which is melted at 720°C in the crucible (2). The preheated concrete dies (3) are inserted into the unit. To prevent aluminum from leaking out, a 2 mm copper foil was cut by hand and placed on top of the flat surface parts of the dies (spacing). When the melt is ready, it is poured into the die, fills the cavity and solidifies under ambient conditions.

2.3 Shock temperature loading tests

The previously described casting process places various requirements on the material: The AAM-UHPC has to withstand the temperature of the hot aluminum melt and must not fail under the short-term extreme temperature gradient. Despite its high strength it must not fail explosively as OPC-UHPC does under high thermal loads (250-300°C) due to the degeneration of the C-S-H-phases and resulting increased water vapor pressure [6].

To simulate the short-term thermal exposition in casting process a shock temperature loading test was set up and compared to a reference sample which had been stored at standard climate conditions.

The shock temperature loading tests were conducted by moving the cubes from storage at room temperature directly into the oven preheated to 700°C, where they remained for one hour. The samples were then removed from the oven and cooled at room temperature until their residual compressive strength was tested.

3 Results and Discussion

AAM-UHPC exhibits high compressive strength of 136,6 N/mm² after 7 days. After 700°C shock temperature loading the AAM-UHPC still had a compressive strength of 22,6 N/mm² which is comparable to the strength of a normal concrete used in construction industry. Anyhow, no spalling occurred up to this temperature of 700°C.

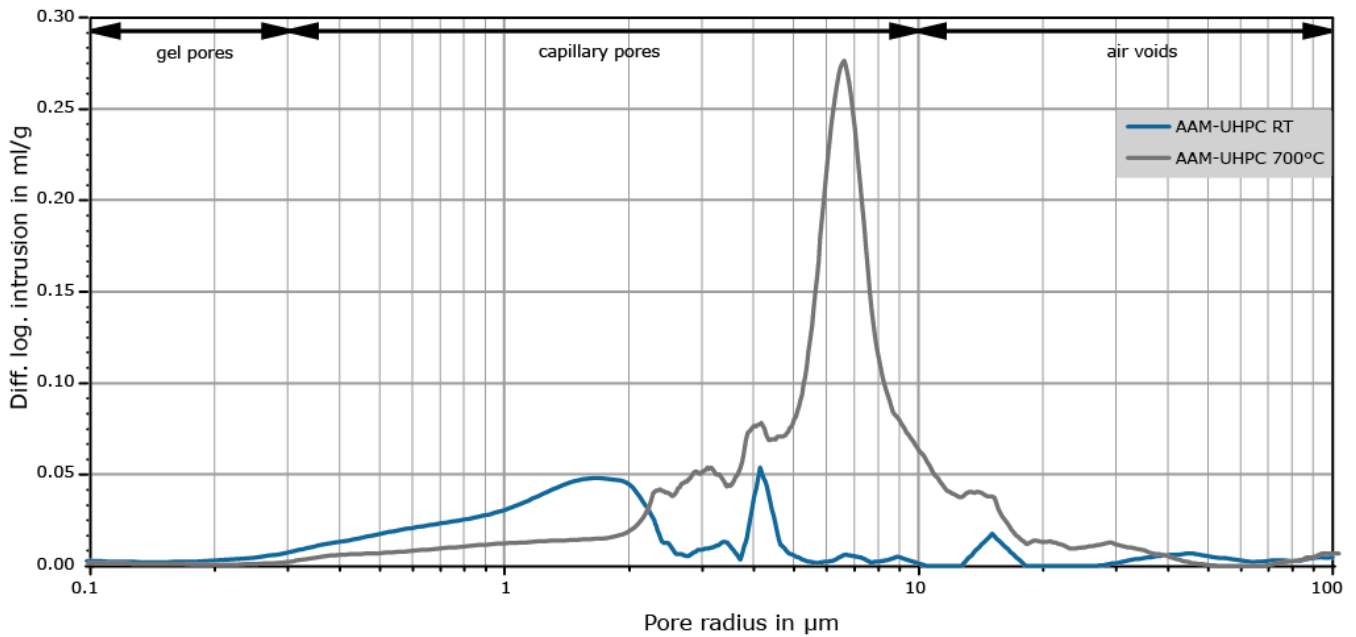


Figure 3 Pore size distribution of AAM-UHPC stored at room temperature (blue) and heat-treated at 700°C (grey), determined with Mercury Intrusion Porosimetry

Mercury intrusion porosimetry was conducted with another series of samples that had undergone the same shock temperature loading. Fig. 3 shows the pore size distribution of the untreated AAM-UHPC sample stored at room temperature (blue) and the sample after shock temperature loading (grey). While the untreated sample has a low total porosity, the porosity is significantly increased after thermal exposure. In the heat-treated sample there is less porosity in the range of the smaller capillary pores under 2 μm . It is assumed that some pore walls have been destroyed by the thermal stress and that the overall pore structure has been coarsened. The rapid increase in porosity in the range of 2 to 20 μm of the heat-treated sample is due to the degradation of the RC fibers at around 300°C, which leave channels in the range of their diameter.

Thermogravimetric analyses (TGA) were carried out with a Netzsch STA 449 F5-Jupiter to investigate the thermal stability of the AAM-UHPC. The material was grinded and heated to 720°C with a heating-up rate of 10 °C/min. At the same time, the mass of the sample was continuously determined. The results of the two measured samples are displayed in Fig. 4.

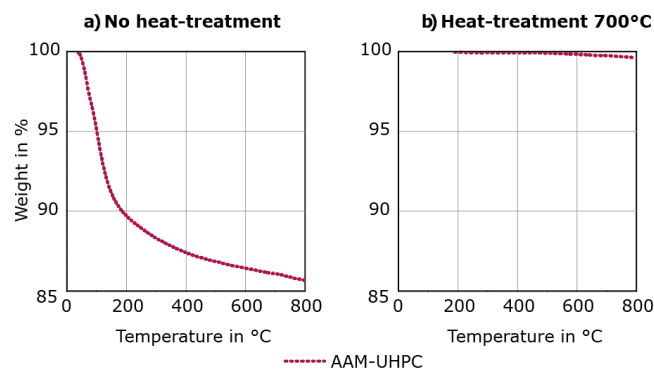


Figure 4 Weight loss of AAM-UHPC after storage at room temperature (a) and heat-treated at 700°C (b)

The sample stored at room temperature experiences continuous weight loss up to almost 15 % when heated up to 720°C. The abrupt decrease until 200°C is due to the loss of incorporated water, which the sample has drawn from the ambient humidity. After that, the curve of mass loss flattens out. The mass loss at elevated temperatures is assumed to be because of the partial degradation of the AAM-UHPC's reaction products (assumed to be mainly C-A-S-H-phases). Here again, an advantage results from the AAM formulation: Unlike OPC-UHPC, AAMs do not contain chemically bound water in their strength-forming N-A-S-(H) phases, except for the C-A-S-H phases, which are formed as reaction products. Therefore, at high temperatures, the strength-forming phases are not immediately and completely destroyed and the AAM-UHPC does not fail explosively.

This thesis could not be confirmed by XRD measurements because the reaction products are mostly X-ray amorphous. When an already heat-treated sample (see 2.3) is heated up again the mass loss is rarely detectable (Fig. 4b) and under 1%. After the sample is heated for the first time (Fig. 4a), most of the mass loss is complete because the incorporated water has evaporated. The use of RC fibers and the network of fiber channels they leave behind allow the water to escape without major damage to the matrix. When the AAM-UHPC experiences multiple thermal loadings the loss of mass and the degradation of the phases do not progress further. This demonstrates the suitability of AAM-UHPC for elevated temperature applications. Dies of this AAM-UHPC were produced for aluminum casting.

To reduce the risk of failure due to high mechanical stresses resulting from a curved surface of the dies, a copper foil was used as a spacer between the corresponding two die parts (Fig. 5).

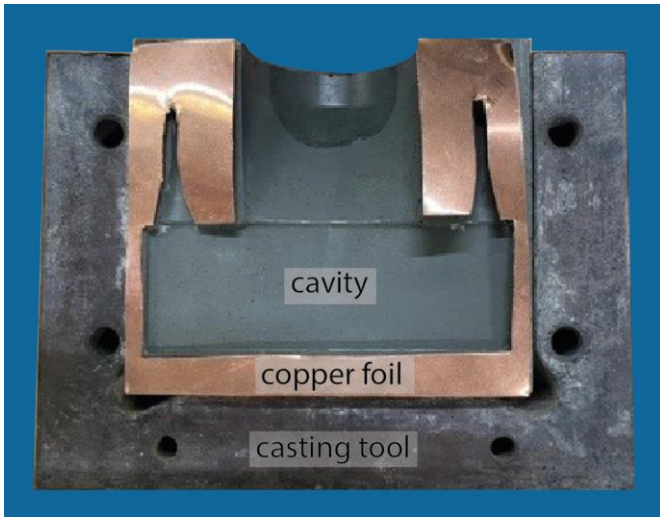


Figure 5 Copper foil as a spacer on one side of the AAM-UHPC die

When the die is produced the surface has small deviation tolerances. The edges of the die, where the two parts lie on top of each other, are not completely even, there are deviations in the range of tenths of a millimeter. The copper foil with a thickness of 2 mm is used as a sealing for this (Fig. 5). The copper foil serves two purposes: It prevents aluminum from leaking out during casting and ensures that the two parts of the die are pressed together evenly. Preliminary tests were conducted without copper foil as a spacer and only a low number of casting cycles were achieved because many dies failed prematurely. It is assumed that the failure of the dies is not only due to thermal shock but also due to punctual pressure on the uneven edges indicating that the occurrence of punctual mechanical stresses accelerates the destruction of the dies.

In preliminary tests the dies failed after 5-10 casting cycles or the surface quality of the aluminum cast decreases, respectively. In Figure 6 the same AAM-UHPC-die is shown after manufacturing (a) and after three casting-cycles with aluminum (b). In (b) the die has not failed, yet, but exhibits multiple irreversible surface defects. Fine cracks are distributed evenly over the cavity which has been in contact with the aluminum melt. Furthermore, the cracks in the upper area show aluminum adhesions. Upon closer examination these are only superficial and can be easily detached. No penetration of aluminum into the die was detected.

The influence of surface defects can be derived clearly from the failure mode around the centrally located pore (Fig. 6 a) and b)): The multiple stresses during the casting process and the filling of the pore with molten metal and subsequent demolding result in spalling near the pore, which continues over the casting cycles (Fig. 6 b). At such surface defects as pores or ridges, the surface quality of the resulting cast components will continue to deteriorate over the increasing number of cycles until it is no longer adequate. It is therefore particularly important to avoid even small surface defects during the production of the dies.

Nevertheless, the surface quality of the cast aluminum component is within the range of conventional steel molds. The requirements for mold tolerances are met.

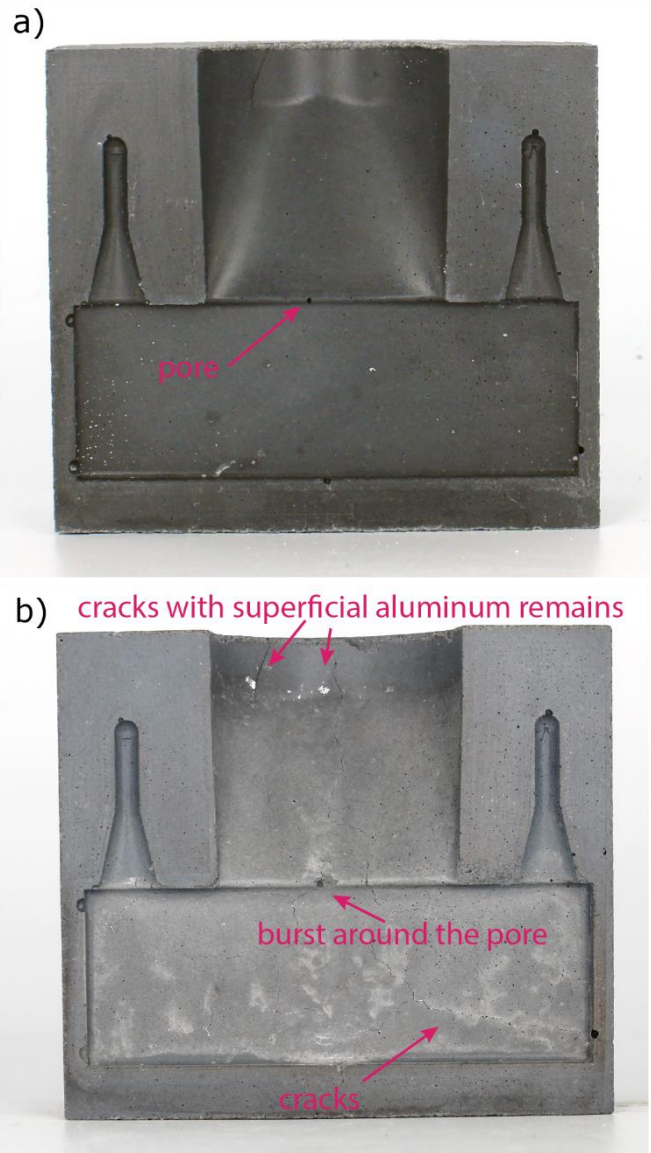


Figure 6 AAM-UHPC-die after manufacturing (a) and after three casting-cycles with aluminum (b)

Another advantage could be the low thermal conductivity of concrete compared to steel: Due to the faster cooling of the melt in steel molds, the pressure must be increased during steel die casting so that the melt completely fills the cavity before it solidifies. This limits the production of thin-walled geometries with steel molds in particular and opens up new possibilities for die casting with AAM-UHPC molds.

4 Conclusion

Although the steel molds can withstand many casting cycles and thus surpass the concrete dies in durability, the use of concrete dies ensures an equivalent surface quality of the cast component and the mechanical properties are improved. In addition, many different geometries can be produced relatively simple, more cost-effective than steel molds and with little effort. Thus, the production of small quantities is more economical than it would be with steel molds.

The die casting can be done with less or even without pressure as the melt solidification is decelerated in comparison to steel molds.

In contrast to steel molds, there is no impregnation of the formwork with aluminum, because there is no metal corrosion, but the concrete dies are merely wetted by the melt.

The thermal stability of the AAM-UHPC has been proven by compressive strength tests and TGA. AAM-UHPC exhibits an adequate compressive strength of over 20 N/mm² after thermal shock loading and the mass loss after repeated heating stabilizes in a minimal range so that no further phase degradations are expected. The absence of chemically bound water in AAM-UHPC increases its thermal stability.

The use of copper foil resulted in an increased number of cycles before the die failed and an increased tightness when the two dies were pressed together. The dies are subjected to less mechanical stress, and shape tolerances at the edges can be better compensated and do not lead to damage to the die.

Due to the use of AAM-UHPC, a low w/b ratio, hydrophobizing agent and the manufacturing process, a low-porosity surface of the concrete die could be achieved, resulting in an adequate surface quality of the cast component. With the help of the RC fibers, the concrete could be made more resistant to thermal stress.

Further investigations are needed on the interaction between the melt and the mineral die, in particular to investigate the influence of the AAM-UHPC die on hydrogen incorporation into the cast component and to ensure the stability of the AAM-UHPC die for a higher number of casting cycles.

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