Thermal diffusivity of organic- and inorganic-bound cores and its influence on the microstructure of Al alloys

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This paper presents a comparative overview of a polyurethane cold box binder system (PUCB) and a silicate-based binder system, Inotec, required for the production of casting moulds and cores. Both technologies are compared in respect of their chemical composition, their core manufacturing process and chemical hardening mechanism. Further performance properties as well as environmental and economic aspects are discussed to emphasize the benefits of inorganic binder systems.

In addition, the microstructure and quality of the aluminium casting are aspects of crucial importance. What is the impact of an organic vs. inorganic binder system on the solidification of the aluminium melt and the microstructural properties of the Al alloy? The goal of this research project was to observe how differences in the thermal diffusivity of moulds and cores based on organic and inorganic binder systems influence cooling rates and solidification times of the aluminium melt as well as dendritic arm spacing in the produced Al alloy castings. In the case of Inotec-bonded cores (inorganic binder system), higher cooling rates and shorter solidification times are observed in correlation with shortened dendritic arm spacing.

Polyurethane cold box process

The requirements placed on casting design of highly complex, thin-wall components, particularly when casting light metals (e.g. aluminium low-pressure die casting), play a significant role in the choice of the binder system. The binder system has a crucial effect on a number of technological, economic and ecological factors. Today, the polyurethane cold box (PUCB) process is the most widely used method of organic core production. In this core and mould production process, refractory moulding materials (e.g. silica sand) are hardened with phenol formaldehyde resins and polyisocyanate derivatives to form a network using tertiary amines as a catalyst. In this process, the terminal methylol groups of the *ortho*-phenol resols and the NCO groups of the polyisocyanate react to form poly-
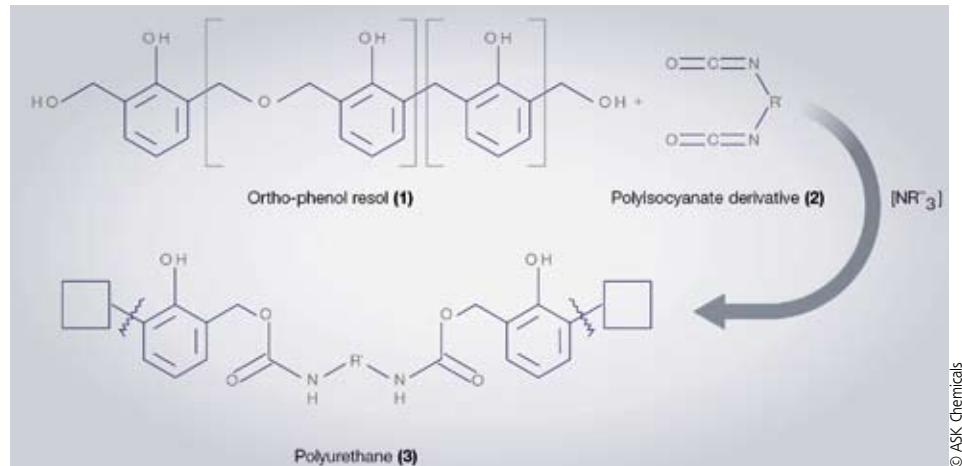

Fig. 1: Schematic reaction of a phenol formaldehyde resin with a polyisocyanate derivative to form a urethane functional group

urethane in a polyaddition reaction (Fig. 1).

Typical polyurethane cold box binder systems can therefore be described as three-component systems (Fig. 2) in which component 1 consists of approx. 50-55% phenol formaldehyde resin and approx. 45-50% solvents, component 2 consists primarily of polymer isocyanate and 15-30% solvents, and component 3 comprises a tertiary amine which acts as the catalyst for the reaction. Frequently used solvents in components 1 and 2 are aromatic and aliphatic compounds as well as polar esters and fatty acid derivatives.

Due to the chemical composition of the multi-component system, the PUCB core production process presents environmental drawbacks. Already during core manufacturing and storage, emissions and odours are perceptible in the form of volatile organic compounds (VOCs) which are present in the binder components 1, 2 and 3. The thermal decomposition (pyrolysis) of the solvents present in the moulds and cores as well as of the polyurethane network generates BTX (benzene, toluene, xylene) and NO_x (nitrogen oxide) emissions and hazardous air pollutants (HAPs) during the casting, cooling and demoulding processes. Any not fully decomposed organic constituents settle as condensate, tar or coke mostly on cool surfaces of the cores or permanent metal moulds (e.g. dies), thus entailing high cleaning and maintenance costs and reducing productivity. Further developments of this conventional PUCB technology include the use of special solvents as constituents of the binder components 1 and 2 to reduce harmful emissions during core production, storage, and casting (e.g. Ecocure
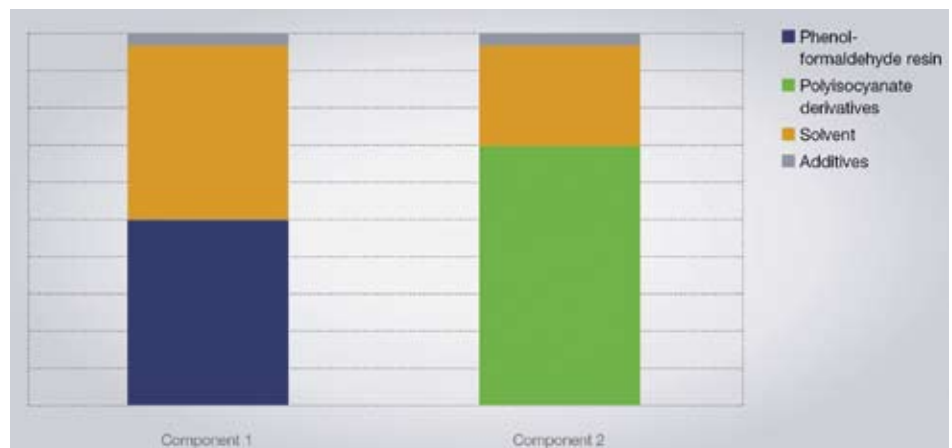

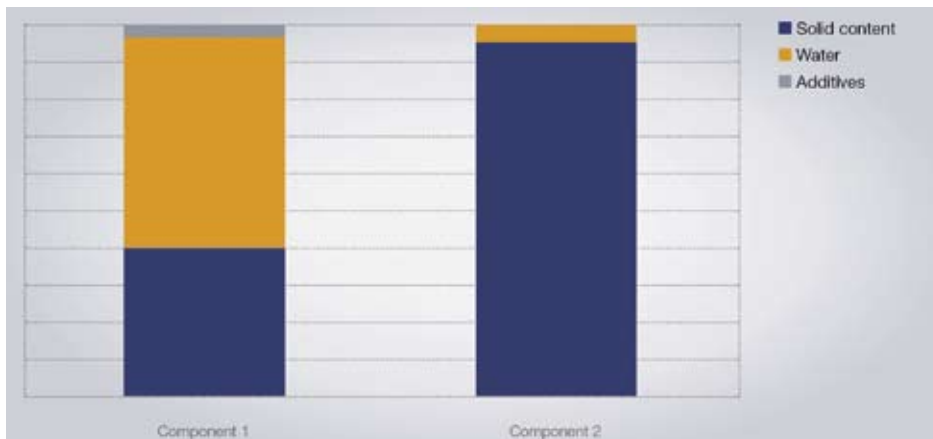Fig. 2: Composition of a typical PUCB binder system

Fig. 3: Composition of a typical inorganic binder system

technology, ASK Chemicals GmbH) [1].

However, the PUCB process offers first and foremost economic advantages: The use of unheated core tools at high production cycle frequencies makes for cost-effective production of cores and moulds at moderate capital expenditure. The high mechanical strength of the core and mould products with low added quantities of the PUCB binder system facilitates a high automation level of the entire production process (manufacture, handling, storage), and ultimately increases the productivity and cost-efficiency of the foundries.

Inotec process

The Inotec technology developed by ASK Chemicals GmbH represents an extremely resource-saving and eco-friendly alternative to conventional organic core production methods. This method has established itself as a high-productivity core manufacturing technology primarily in aluminium low-pressure and gravity die casting used in the production of cylinder heads and crankcases.

The Inotec technology uses a two-component binder system: component 1 (Inotec binder) is based on a modified, aqueous alkali silicate solution; component 2 (Inotec promoter) can be described as a solid blend of synthetic and mineral materials that have a significant influence on the properties (e.g. initial strength, thermal stability) of the manufactured moulds and cores (Fig. 3).

For the production of inorganic moulds and cores, the mould material mixture consisting of refractory material (e.g. silica sand) and the inorganic binder system is cured at temperatures from 130 to 200 °C by heating the core box tools and introducing compressed air heated to over 100 °C. The physical and chemical curing mechanism comprises the evaporation of the water from the mould material mixture and the thermal initiation of a polycondensation reaction which, by elimination of water and formation of Si-O-Si bonds, results in the formation of a three-dimensional network of SiO_4 tetrahedrons [2].

The aqueous alkali silicate solution (component 1) contains monomers and dimers as well as polymer silicate anions, a part of which are present in solution in the form of colloidal particles stabilized by the presence of an electrostatic bilayer. By changing the external state, e.g. by elimination of water during the core and mould production, the chemical equilibrium is shifted towards the condensation products and molecule enlargement. In this process, a continuous enlargement of particles (sols) or the agglomeration of individual particles to chains and networks (gels) is observed, depending on the pH value of the alkali silicate solution.

The three-dimensional binder framework contains network formers (e.g. SiO_2) and network modifiers (e.g. Na_2O). The network forming constituents of binder component 2 are partly integrated into the basic silicate framework via reactive groups on the particle surfaces of the mineral and/or synthetic raw materials, and thus increase the speed of the chemical curing reaction of the binder system.

The Inotec core production method offers primarily ecological benefits: the absence of harmful emissions during core production and storage, as well as during the casting, cooling and demoulding processes makes it possible to forgo the installation of air treatment systems. This is a well-known advantage of inorganic binder systems. An environmental lifecycle assessment comparing the Inotec binder system with a PUCB binder system has confirmed the environmental friendliness of the former [3]. In serial production (e.g. aluminium low-pressure die casting), the absence of condensate formation in the casting process reduces the amount of cleaning required for the permanent moulds (dies). It thus enables not only a higher casting output, but also selective cooling which, in turn, allows control of the solidification behaviour of the aluminium melt. This gain in productivity is offset by higher investment and energy costs for the provision, maintenance and operation of the heated core box tools.

Method for determining the thermal diffusivity of organic- and inorganic-bound moulds

The thermal diffusivity α expresses the ratio of thermal conductivity λ to thermal capacity $\rho \cdot c_p$ of a material of density ρ and specific heat c_p. The determination of the thermal conductivity of organic- and inorganic-bound moulds is carried out by the hot wire or hot strip method [4]. Here, a heat source emits a heat impulse which diffuses along a thermal gradient to the heat sink where it generates a location- and time-dependent temperature
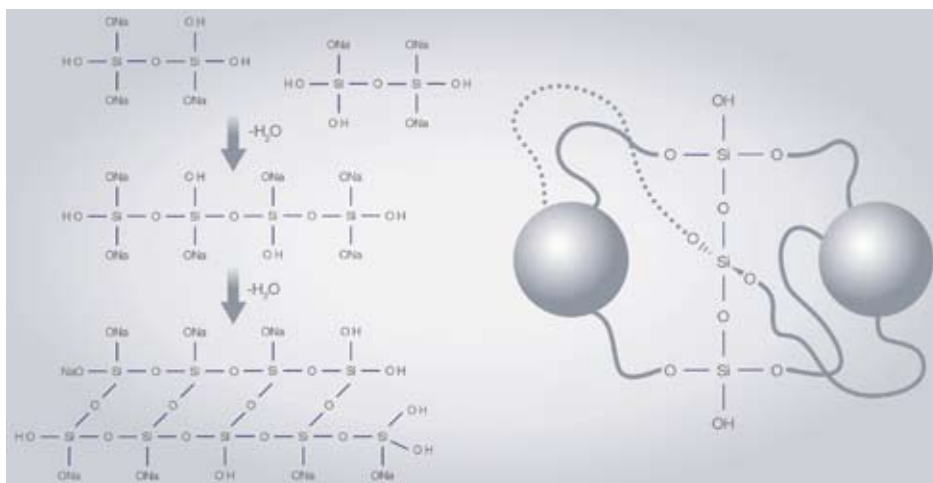

Fig. 4: Polycondensation of alkali silicate solutions with formation of a three-dimensional SiO4 network (left side) and schematic integration of network-forming components of the Inotec promoter in the silicate network (right side)

increase $\Delta T(r,t) = T(r,t) - T_0$. Thus, when the molten aluminium is poured into the mould at time point t_0, a heat impulse H is generated which diffuses through the mould and is captured due to a rise in temperature at a thermocouple (temperature sensor) located at a defined distance r to the aluminium melt (heat source) (Equation 1):

Equation 1: Time- and location-dependent temperature rise

$$\Delta T(r,t) = \frac{H}{4\pi Lat\rho c_p} \, exp \left(-\frac{r_1^2}{4at} \right)$$
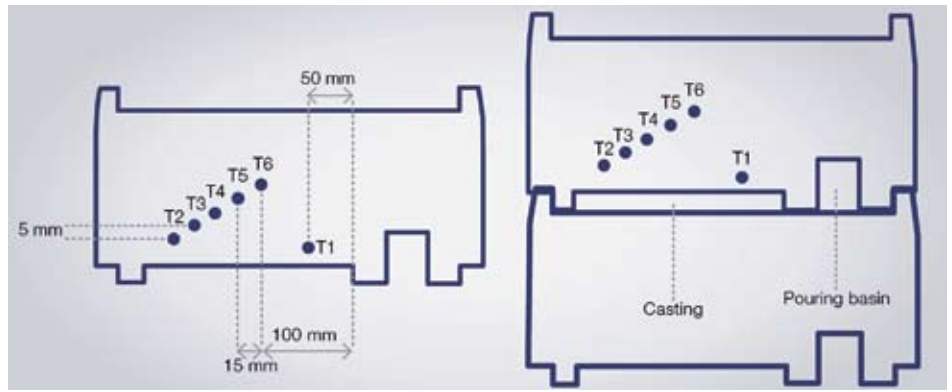
L = length of the heat source

Fig. 5: Arrangement of the temperature sensors on the topside of one half of the mould (top view, left) and consolidation of the mould package (top view, right)

Regardless of the amount of heat applied, the respective peak temperature will be reached at the time t_{max} (Equation 2). By determining the time difference Δt_{max} between capture of the peak temperatures of two temperature sensors located at different distances $r1$ and $r2$ ($r2 > r1$) to the heat source, it is possible to calculate the thermal diffusivity a.

Equation 2: Calculation of thermal diffusivity

$$t_{max} = \frac{r_1^2}{4a} \quad \Delta t_{max} \frac{(r_2^2 - r_1^2)}{4a} \leftrightarrow a = \frac{(r_2^2 - r_1^2)}{4\Delta t_{max}}$$

Description of the test for determining thermal diffusivity

The moulds used to determine the thermal diffusivity were manufactured using silica sand of a defined granular distribution according to the organic and inorganic core production processes described in Sections 1 and 2. The vertically divided core box tool is heated via external full-surface hot plates and the escaping air is discharged to the outside via core box vents. The moulds were utilized immediately after manufacturing.

The test setup for determining the thermal diffusivity consists of one vertically divided mould package made up of two identically designed moulds joined by external locking mechanisms. The design of the moulds is approximately rectangular and each mould features a square cavity with a pouring basin on one side. The other side of the mould is designed as a flat surface which closes the square cavity on the face of the mould package. The rectangular casting with approximate dimensions 20.5 x 18.0 x 5.8 cm is formed by filling by gravity casting. After core manufacturing, a total of six temperature sensors were inserted manually by drilling on top of one half of the mould (Fig. 5). The temperature sensor T1 was placed in a quartz glass tube in the square cavity of the mould package at a distance of 50 mm and depth of 60 mm, measured from the margins of the casting cavity, to

measure the cooling rate of the aluminium melt. The other five temperature sensors (T2-T6) were integrated in the core package, each 15 mm apart and at a depth of 60 mm, measured from the margins of the casting cavity. Here, the distance of the temperature sensor T2 to the aluminium melt measures 10 mm and the following temperature sensors were each positioned at a distance of 5 mm to the previous one, thus resulting in a diagonal arrangement of the measuring points. The recording of the temperature profiles took place at time point t0 which corresponds to the time at which the molten aluminium was poured into the mould package.

In a pot-type furnace, 75 kg of the alloy AlSi10Mg(Cu) were charged and heated to the casting temperature of 745 °C ±5 °C. After melting, melt refinement took place by rotation degassing (impeller, 15 min, argon). Using a pouring spoon, the aluminium melt was poured manually at a constant speed into the prepared mould packages at time point t_0 (start of temperature measurement). The capture of the temperature profiles was discontinued after five minutes and after reaching a temperature within the casting of < 400 °C. The casting was cooled overnight in the mould package at standard conditions and then demoulded and cleaned.

For analysis of the secondary dendritic arm spacing (SDAS) according to VDG guideline P220, the castings were each divided into six metallographic samples of dimensions 30 x 25 x 20 mm. The SDAS is primarily influenced by the local solidification time (SDAS = $k \cdot tE^{1/3}$);

this means that fast solidification generally results in lower SDAS values and hence good mechanical properties of the obtained casting are assured.

Results of determination of temperature diffusivity of PUCB- and Inotec-bonded moulds, and comparison of secondary dendritic arm spacing

Figs 6 and 7 show the cooling curves of the aluminium melt (T1) and the temperature profiles of the measuring points integrated in the moulds (T2-T6) of the PUCB- and Inotec-bonded mould packages. The recorded values are based on simultaneously performed duplicate determinations in order to minimize statistical and systematic errors.
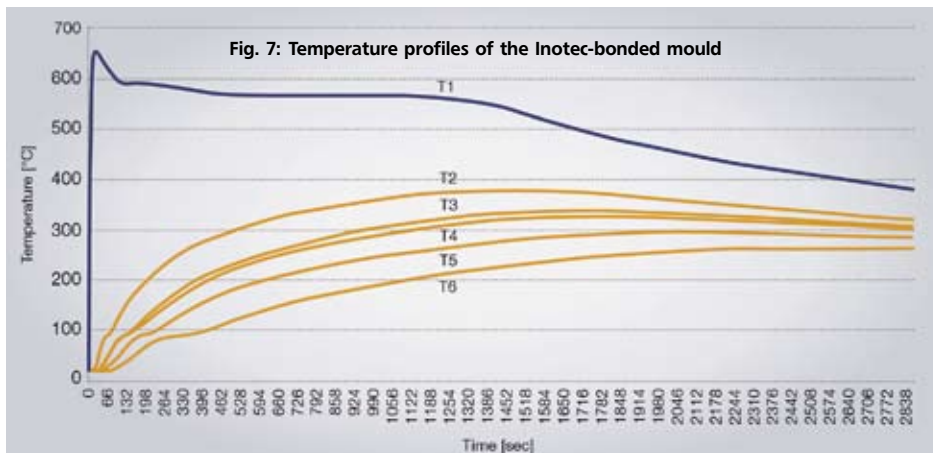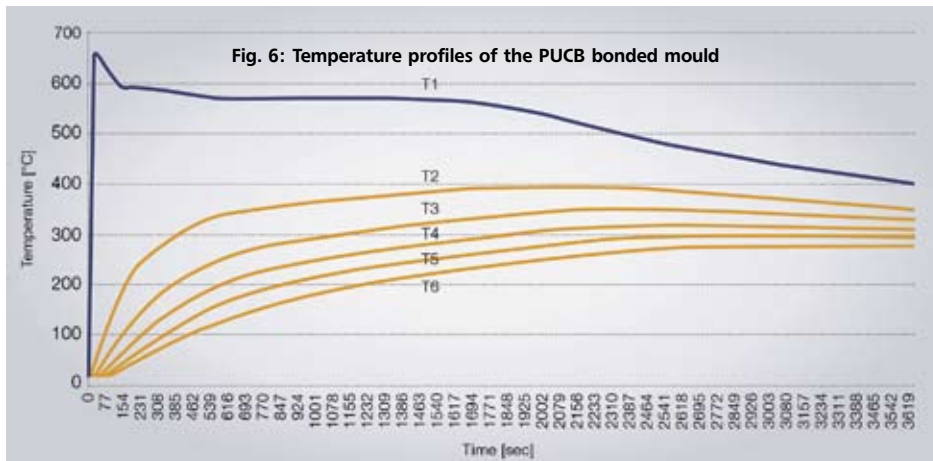
The liquidus and solidus temperature can be calculated from the specific cooling curve of the aluminium melt, and this in turn allows conclusions to be drawn on the solidification behaviour of the melt. The local solidification time of the aluminium melt is calculated as the temporal difference between beginning and end of solidification. The calculated liquidus ($T_{Liquidus}$) and solidus ($T_{Solidus}$) temperatures as well as the calculated solidification

Table 1: Comparison of local solidification times for aluminium melts in the PUCB- and Inotec-bonded moulds

	PUCB mould	Inotec mould
$T_{Liquidus}$ [°C]	591	588
$T_{Solidus}$ [°C]	532	530
t_E [sec]	1915	1375

Table 2: Peak temperatures at the measuring points T2-T6 in the PUCB- and Inotec-bonded moulds

Spacing	PUCB mould		Inotec mould	
	T_{max} [°C]	t_{max} [sec]	T_{max} [°C]	t_{max} [sec]
r_2 (10 mm)	398.8	2092	379.2	1480
r_3 (15 mm)	349.7	2413	336.5	1640
r_4 (20 mm)	319.5	2741	325.0	1735
r_5 (25 mm)	298.2	3021	294.6	2094
r_6 (30 mm)	279.7	3253	263.8	2525

Fig. 6: Temperature profiles of the PUCB bonded mould

Fig. 7: Temperature profiles of the Inotec-bonded mould

The thermal diffusivity of the PUCB-bonded mould increases with growing distance to the aluminium melt. This phenomenon could be due to the high level of pyrolysis of the organic binder network in the direct vicinity of the aluminium melt. By comparison, the thermal diffusivity of the Inotec-bonded mould is already doubled in the first spacing interval $r3$-$r2$. In the next spacing interval, a thermal diffusivity peak can be observed which falls to a constant minimum with increasing distance to the aluminium melt.

The comparatively higher thermal diffusivity values of the inorganically bonded mould display a highly consistent correlation with the shorter solidification times of the aluminium melt. The short solidification time of the aluminium melt in the Inotec-bonded mould has a significant impact on the secondary dendritic arm spacing (SDAS) of the obtained casting (Fig. 8). The SDAS values of the casting from the PUCB-bonded mould range from 79 µm to 99 µm, while those obtained for the casting from the Inotec-bonded mould are in the range from 66 to 86 µm. On average, the SDAS values observed in the casting from the Inotec-bonded mould are approximately 9.8% lower.

References

[1] Vacelet, P. H., Priebe, C., Muniza, J.: Neue Solventless Cold-Box-Technologie reduziert Emissionen während des gesamten Gießereiprozesses (*A New Solventless Cold-Box Technology Reduces Emissions in the Foundry Process*), Giesserei-Rundschau, 60, 2013, 67-70.
[2] Iller, R. K., The Chemistry of Silica, John Wiley & Sons, 1979.
[3] Dr. Deters, H., Dr. Müller, J.: Ökobilanz-Vergleich von Inotec, dem anorganischen Bindersystem, mit einem klassischen Cold-Box Bindersystem (*A comparative Environmental Lifecycle Assessment of Inotec, the Inorganic Binder System and a conventional Cold Box System*), Giesserei-Rundschau, 61, 2014, 74-76.
[4] Patentschrift (*Patent Specification*) DE 102 06 275 B4

times (t_E) are listed in Table 1. The aluminium melt in the Inotec-bonded mould solidifies at a significantly higher cooling rate than the melt in the PUCB-bonded mould.

A comparison of the temperature profiles of the integrated measuring points could provide an explanation for the shorter solidification time of the aluminium melt in the Inotec-bonded moulds. The temperature profiles of the Inotec-bonded moulds exhibit an approximately temperature plateau for the evaporation enthalpy of water. In general, Inotec-bonded moulds have a water content of approx. 0.1-0.2% after core manufacturing. The water contained in the mould package evaporates due to the thermal energy of the aluminium melt during the casting and cooling process so that heat is continuously removed from the melt, thus resulting in the observed shorter solidification times. This evaporation process can be traced by a slight rise in the respective temperature curve.

The greater the distance of the measuring points T2-T6 to the aluminium melt, the lower the peak temperatures exhibited by the temperature curves of the PUCB- and Inotec-bonded moulds, and the later these are captured (Table 2). In comparison, the peak temperatures of the Inotec-bonded mould are consistently lower than those of the PUCB-bonded mould. Taking the time difference Δt_{max} between capturing the peak temperatures of two measuring points located at different distances $r1$ and $r2$ ($r2 > r1$) to the aluminium melt into account, the thermal diffusivity was calculated (Table 3).

Table 3: Calculated thermal diffusivity of the PUCB- and Inotec-bonded moulds

Spacing interval	PUCB mould $a * 10^{-6}$ [m^2/sec]	Inotec mould $a * 10^{-6}$ [m^2/sec]
r_3-r_2	0.097	0.195
r_4-r_3	0.133	0.461
r_5-r_4	0.201	0.157
r_6-r_5	0.296	0.160

Fig. 8: Secondary dendritic arm spacing (SDAS) of the metallographic samples