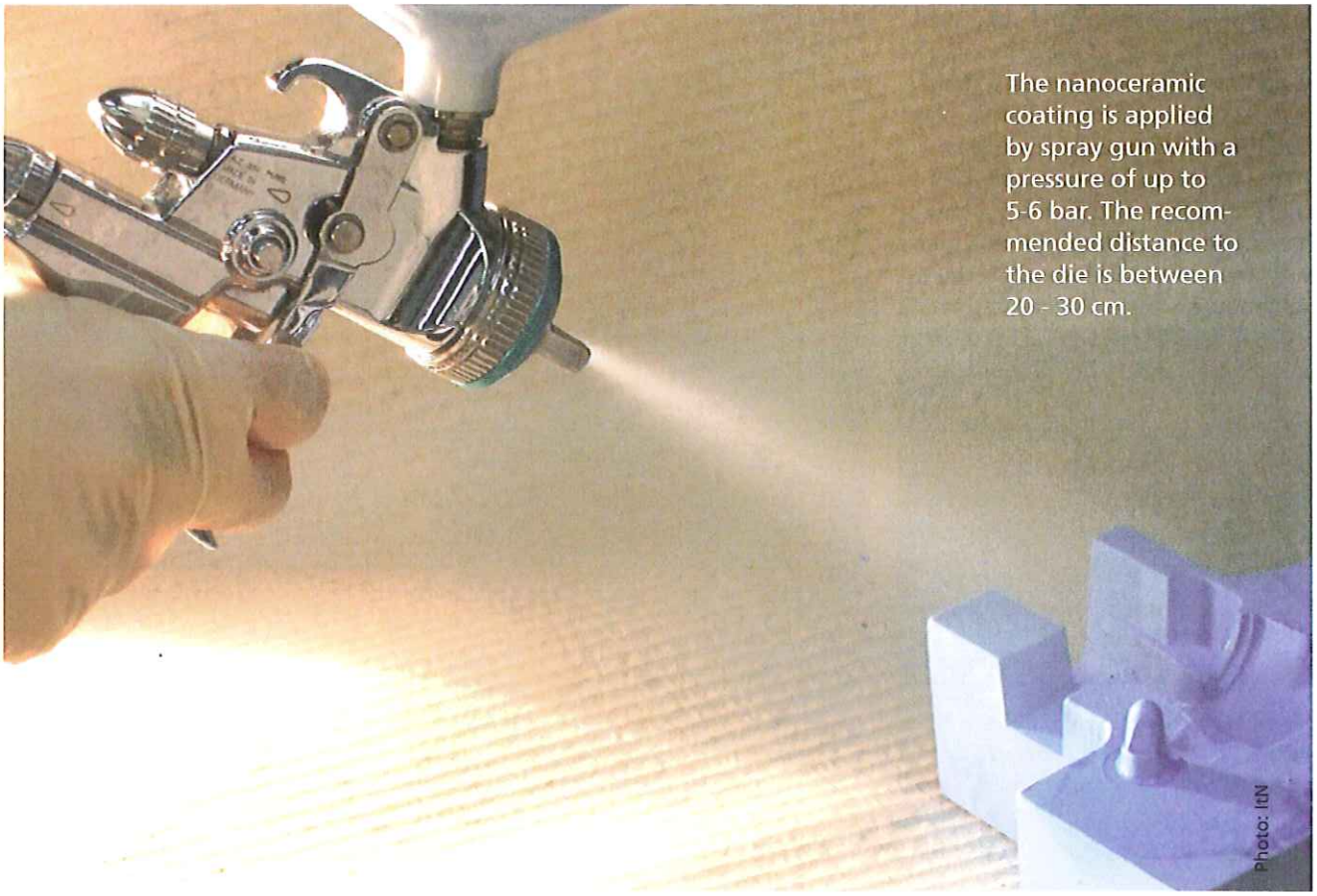

The nanoceramic coating is applied by spray gun with a pressure of up to 5-6 bar. The recommended distance to the die is between 20 - 30 cm.

Photo: ItN

Authors: Frank Meyer, Stefan Faber, Jörg Vossen, ItN Nanovation AG, MetCast, Saarbrücken

Nanoceramics in aluminium permanent mould casting

A thin protecting top layer based on a nanoceramic binder is an excellent protection against molten metal and stabilizes the aluminium permanent mould process

Ceramics are considered to be robust and inert to chemical attack and thermal exposure. But the traditional way to achieve a ceramic is to sinter metal oxides, e.g. ZrO_2 at high temperatures of up to 1700 °C.

By using nanoscale ZrO_2 as a ceramic binder, the sintering temperature can be lowered significantly to a few hundred degrees.

Nanocomp MetCast products are coatings that make use of this effect to achieve a low-sintering ceramic layer on metal or mineral substrates. Initially, nanoceramic products were developed to provide a permanent and excellent protection against molten metal, combined with good release properties. Thus, e.g. with metal production (ingot casting), a stunningly increased service time of up to four weeks could be achieved. Now these findings have been transferred to permanent mould casting. Although purely insulating coatings can be provided, the simplest strategy to benefit from this new technology is to protect the existing mould release agent (base layer) with a thin protecting top layer based on the nanoceramic binder.

Minimization of the functions of mould release agents

In aluminium permanent mould casting, the release agent must provide roughness and insulating prop-

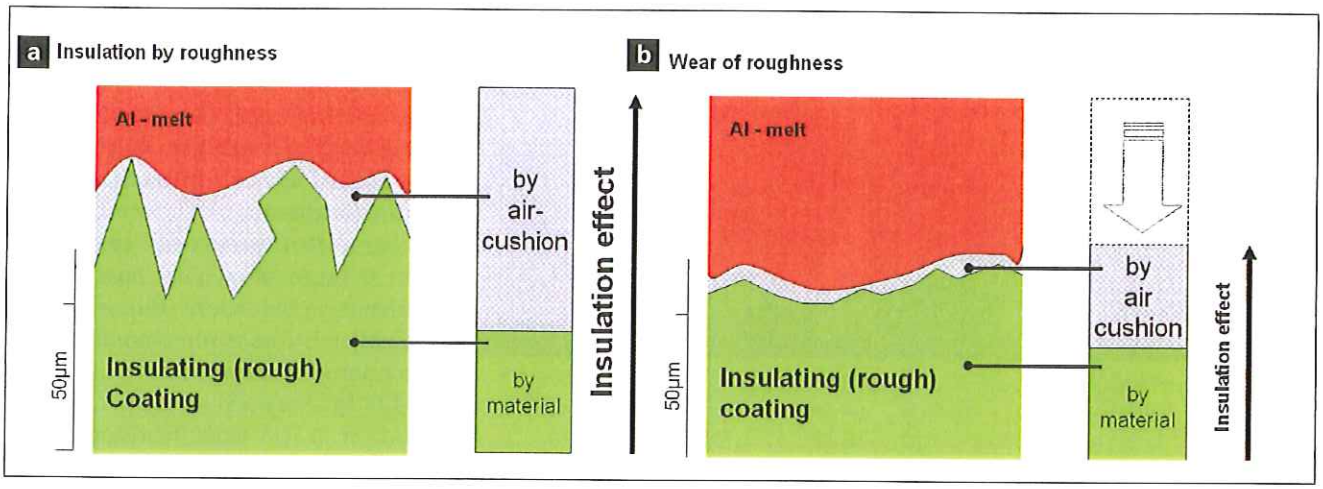

Figure 1: Insulation due to roughness (a), Impact of wear (b)

erties in addition to its release effect. The roughness is highly important for two reasons. In the first place, it ensures good flow properties by scraping off the oxide film that is constantly forming on the molten metal surface. Secondly, the roughness achieves extremely good insulation due to an air cushion that forms between the release agent and the molten metal (**Figure 1a**).

With conventional release agents, heat transmission between the molten metal and the die is largely minimized by this air cushion. It is the roughness that produces between 40 % and 80 % of the release agent's insulating properties [1]. In addition, the roughness supports mould venting.

Standard release agents can implement these ideal conditions within the mould – but only very briefly. With every single casting, the conditions deteriorate due to wear or chemical attack from the molten metal. Whereas in open moulds a new mounting or reapplication of the release agent is required after the separating layer has completely worn away, in aluminium permanent mould casting the release agent must be reapplied during operation when the roughness of the release agent has been removed by abrasion in selected spots or over large areas (**Figure 1b**). The layer itself is predominantly still present and the constant reapplication of the release agent during spot fixing may lead to a build-up of layer thickness, and finally to peeling off of the coating. At this point, if not before, it is necessary to blast-clean the layer and completely reapply the coating. This leads to fluctuations in the process and reduced efficiency.

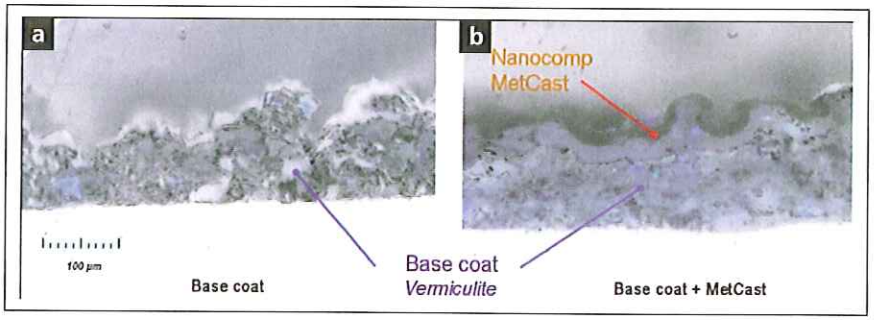

Figure 2: MetCast coating as a thin layer

The temperature of the die – if it is not actively controlled – is therefore a function of the temperature of the molten metal, mass, clock rate and heat transmission from the molten metal to the die. It stabilizes after a few castings. Interrupting the process to reapply the release agent disrupts this equilibrium. In most cases the wear mechanisms mentioned above are the reasons for a high frequency of subsequent misting or recoating.

Principle of operation behind the nanoceramic coating

In pig casting and in applications such as separating agents in refractory troughs and launders, it has been shown that with the Nanocomp Metcast nanoceramic coating a service life of several hundred hours of use can be achieved even with layer thicknesses of just a few micrometers. This resistance to wear with extremely thin layer thicknesses has led to the concept of protecting the roughness of conventional release agents in permanent die casting with an extremely thin ceramic film. This principle also meets the requirements of those customers who tend to avoid having to redefine insulating and surface properties regularly. The final goal is the prevention to repeat the high development effort required for the selection of the suitable release agent and the definition of application parameters.

The principle of operation behind nanoceramic coatings for die casting is a thin protective envelope which conserves and does not impair the surface structure of the insulating mould release agents (**Figure 2**).

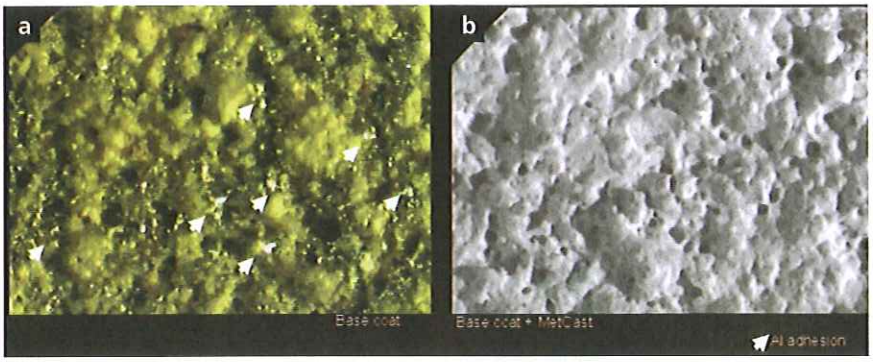

Figure 3: Aluminium adhesion on non-protected base coat

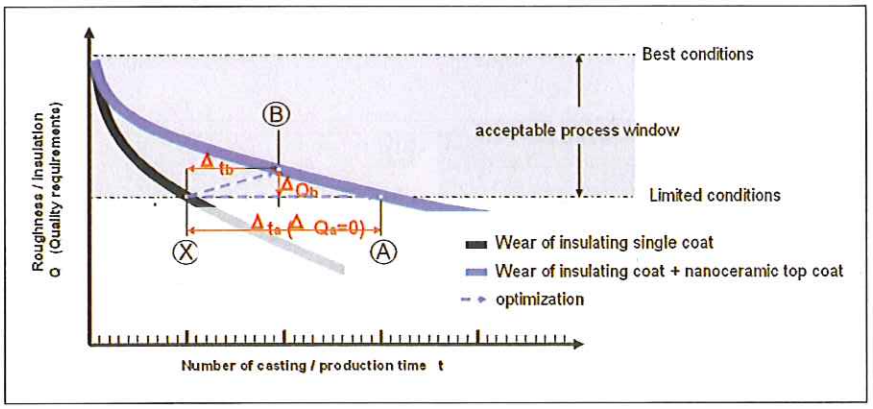

Figure 4: Graphs / wear of roughness

Base release agent is not impaired

The function of the base release agent could theoretically be impaired if the ceramic film changed the surface structure significantly. Measurements of the surface structure and roughness prove that this does not occur. Systematic laboratory research has also determined that there are no deviations in the insulating properties.

An additional influence could result from the modified wetting behaviour. The nanoceramic coating contains a high percentage of boron nitride, which induces strong non-wettability towards molten aluminium. During application this provides outstanding separating properties. Both coatings shown in **Figure 3** were subjected to 10 casting cycles.

Baked-on aluminium can be seen on the unprotected coating (Figure 3a) only. No aluminium contamination is seen on the coating protected with Nanocomp MetCast (Figure 3b). Such adhesions eventually may bond to the surface of the mould and finally destroy the coating.

Extension of service life

The service life of a coating primarily depends upon two general factors: the stress placed on the coating, and the sensitivity of the casting to fluctuations with respect to insulating and surface properties. Service life may therefore vary from die to die by several orders of magnitude. With the use of nanoceramic coatings though, resistance to abrasion is noticeably increased.

According to results gained by actual use, an average improvement of 300 % over normal service life can be expected: The total range varies between 150 % and 700 % improvement. A deterioration of service life (correct application provided) has not been observed yet. The parameters that are controlled through the die coating are impaired to a lesser extent by the stress loads; the process is more stable. The benefits of this stabilizing effect depend on the process and may vary widely. In general, this results in fewer interruptions within the process. Full exploitation of the benefit of productivity is shown in **Figure 4** with an extension of service life from X to A with a significant Δt(a).

In other processes, plant-mandated overhauls require operation to be interrupted before the coating has completely lost its function. The foundryman then profits from process stability in a way where he can allow the process to run with smaller windows of tolerance. For each Δt there is one ΔQ (Figure 4).

This type of use corresponds to perfection. The product cycle, whose lifespan is limited by wear on equipment elements, is not interrupted for blast-cleaning and reapplying of the coating. It will complete the cycle uninterrupted, without the coating reaching the limits of its function. When the borderline settings are not reached, the risk of rejects and tool wear are also reduced.

Results in actual use

The principle of operation and performance of MetCast MM12 was proven in the Mercedes-Benz light-metal foundry in Mettingen, Germany. Each week, an average of 750 NGV (New Generation V-Engines) cylinder heads (**Figure 5**) is produced per die with a gravity die-casting method. The dies normally have to be blast-cleaned after 300 castings.

The aim in using MetCast MM12 was to achieve a service life of 750 parts. For the release agent this implies enduring the entire overhaul cycle of one week without any loss of quality. When the production was interrupted after one week, the coating was still in good condition. The gravity die caster can therefore produce for one week without having to clean the dies, while the required product quality is ensured. The fact that the coating still remains within the process window at the end of the specified overhaul cycle, works to the benefit of product quality and protects tool equipment.

In a different application, aluminium wheel manufacturers also bene-

fited until the end of the overhaul cycle from the reduced wear provided by a nanoceramic coating and from the stability of the product quality, thereby avoiding costs associated with rejects and reworking.

Because the coating remains within the process window until the end of the overhaul cycle with regard to its protective and quality functions, a better protection of the tool equipment is provided. Wheel manufacturers prefer using the system with the AlSi7 alloy for this reason alone.

This technology can also be used in the non-automotive area. For example at Stihl in Brazil, products for small combustion engines are manufactured. Fast deterioration of the release agent is highly critical here because it is not possible to restore the function of the release agent through subsequent misting. The release agent is subject to very high stress loads by the cylinder ribs. The application of Nanocomp MetCast increased the service life of the coating by 150 – 200 %. Now the service life usually lasts until the plant-mandated interruption of production.

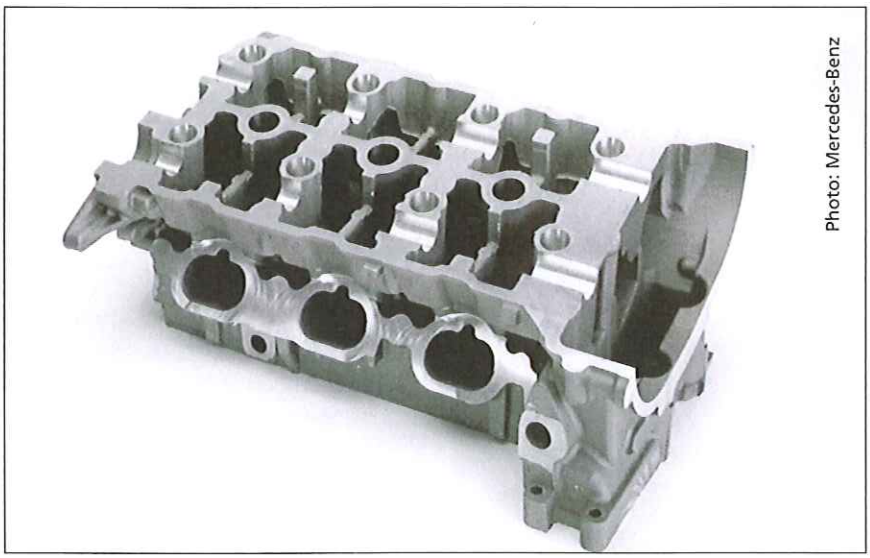

Figure 5: Mercedes Benz NGV cylinder head, manufactured with Nanocomp MetCast MM12

Operating principle of nanoceramics

Chemical nanotechnology is involved with the technological utility of modified properties of materials that exist in defined nanoscale sizes, i.e. smaller than 0.1µm. One industrially available nanoscale material is ZrO_2, which is already used frequently in refractory technology in its coarser microcrystalline form. While this substance in its microcrystalline form sinters into a ceramic at temperatures well above 1500 °C, the sintering temperature for nanoscale ZrO_2 particles can be lowered to a few hundred degrees. The temperature required to sinter ZrO_2 particles therefore lies in the temperature range reached during the process of aluminium casting. This sintering effect is exploited in such a way that the ZrO_2 is employed as a nanoceramic binding agent to solidify the layer. A selection of other binding agents and functional additives as well as thermochrome pigments and, if needed, boron nitride, provide a palette of products for a wide range of applications. Of particular importance is the use of aluminium titanate, which provides the necessary abrasion resistance whilst featuring good demoulding and chemical properties.

Conditions of use

One objective in the development of nanoscale ceramic coatings for die casting was to avoid a disturbance of existing workflows, procedures and modes of action. As a precondition, no increase in special requirements on behalf of plant technology or qualifications of employees could be demanded. This goal has been achieved.

The described system requires the use of a conventional base release agent to produce insulating properties and roughness and to ensure a primering effect (**Figure 6**). On bare uncoated metal, adhesion of the Metcast system is insufficient at high die temperatures. On an existing waterglass-based release agent, a mist coating can be applied at temperatures up to 450 °C. But this procedure is limited to base release agents that do not have a water-repelling effect. Hence the nanoceramic layer does not adhere to graphite, for example. A high degree of care is also required during its first application: an extremely thin layer has to be applied. So far, it has always been possible to learn the correct application of the coating either on the first go or after a short training phase. Not all conventional release agents have been tested yet for compatibility with this system.

The nanoceramic product preferred for use as a top coat has a high boron nitride content. Therefore, the greatly reduced wettability can prompt an increased thermal distance between the molten metal and the die. This can strengthen the insulating properties.

Two die casters reported reduced die temperatures. While one caster welcomed this development, the other one had to switch to a product with a lower boron nitride content. The multitude of conventionally available release agents and their varying chemical composition does not permit a one-size-fits-all solution. With the great variety of practical applications, it is however a fact that no change to the wettability behaviour of the base release agent is perceptible, and the changes caused by the nanoceramic coating offer significant advantages. A very important criterion is the successfully performed sintering process which requires a coating temperature

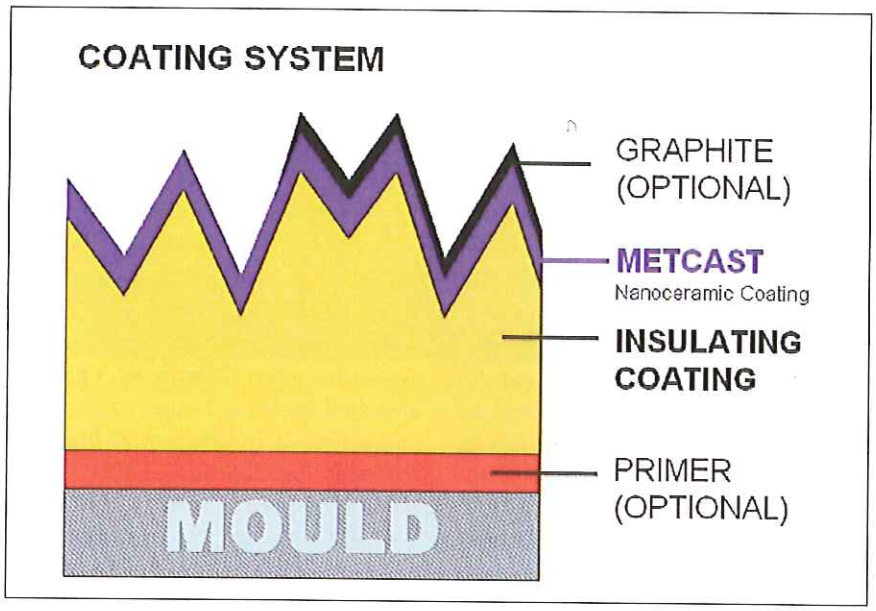

Figure 6: Principle of nanoceramic coating system

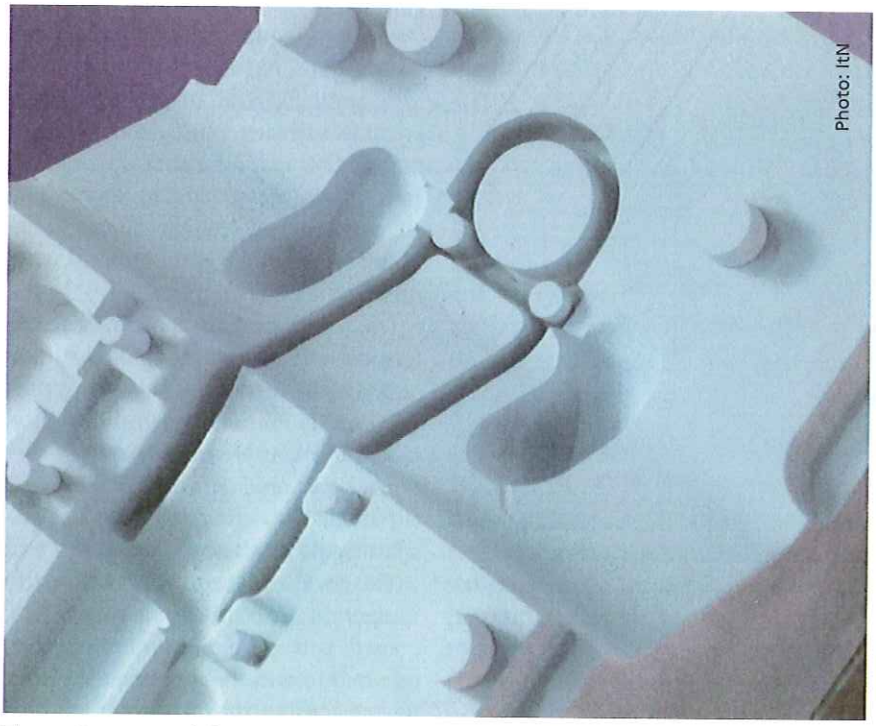

Figure 7: Successful sintering is shown by a thermochrome colour change of the coating

of 400 °C. Since the nanoceramic layer is situated between the molten metal and insulating release agent, it is generally unproblematic to fulfil this precondition. An irreversible thermochrome colour change of the coating indicates that the sintering process has been completed successfully (**Figure 7**).

No build-up of condensate

Highly cored castings in permanent mould applications rapidly lead to a build-up of condensates originating from pyrolysis products from the amine-phenolic binder system of the sand cores. Consequently, the roughness of the surface is not destroyed by mechanical wear but by smear up of the coating roughness by condensates. Within a few castings the coating surface turns brown or even black, and a regular casting process is no longer possible. Surprisingly it has been found that nanoceramic coatings with hydrophobic properties can assist in mitigating this problem. One outstanding feature of Nanocomp MetCast is the low wettability against these condensates. In cylinder head production with cold box core use, the build-up of condensates could be reduced considerably.

Further fields of application for nanoceramic materials

Nanocomp MetCast is already being used as a pure release agent and as protective coating. Almost all metallic and mineral substrates that require protection from aggressive molten light metal can be coated with a nanoceramic product while at the same time an outstanding release effect must be provided. These technical surfaces include troughs, tools, ladles, launders, furnaces, casting tables, etc.

When used in ceramic troughs, for example, a service life of more than 200 hours of use (flowing molten metal) has been observed. This corresponds to a five to seven-fold increase over the service life of a competing high-quality boron nitride product.

Summary

When a nanoceramic coating is applied on top of a conventional die coat in a die, it is possible to multiply the service life of the commercial coating by a factor of up to seven. This opens up diverse possibilities for utilization to the foundryman. In an ideal situation, the foundry is able to produce a complete series without reapplying or reworking the release agent before plant-mandated interruption while still operating within the prescribed process window. This improves productivity and product quality and guarantees the protection of equipment. Newly defined process quality is the paramount argument for the use of this technology. If specific conditions are also to be fulfilled,

the use of Nanocomp MetCast can be considered to be without compromise, since it does not affect any established procedures. Nanoceramic products for metal production and brass casting, both on metallic and ceramic substrates have already been established successfully. Therefore it can also be assumed that the latest nanoceramic product will further increase the efficiency of the system despite the necessity of making slight changes in the standard processes. Not only does this optimization boost process efficiency, but the drastically reduced consumption of the conventional separating agent proportionally leads to an equally drastic reduction of release agent-related fine and ultrafine particulate emissions with a noticeably positive impact on the environment and working conditions.

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