Influence of Ceramic Foam Filters with Al₂O₃ Nanocoating on the Aluminum Filtration Behavior Tested With and Without Grain Refiner

CLAUDIA VOIGT, BEATE FANKHÄNEL, BJÖRN DIETRICH, ENRICO STORTI, MARK BADOWSKI, MARGARITA GORSHUNOVA, GOTTHARD WOLF, MICHAEL STELTER, and CHRISTOS G. ANEZIRIS

In industrial applications, filter materials are often chosen according to cost as well as their processing and thermomechanical properties, but rarely in terms of their behavior during filtration, which is largely due to there being insufficient information available on the influence of filter materials and surface quality on filtration behavior. In this study, the manufacture of functionalized Al₂O₃ nanofilters was investigated, along with their filtration performance in short- and long-term filtration trials. In addition, sessile drop tests were performed to measure the contact angle of the nanofunctionalized materials, and yielded an approximately 10 deg (11 pct) higher contact angle for nanocoated materials sintered at 800 °C and 1250 °C than for those sintered at 1600 °C and an approximately 23 deg (23 pct) higher contact angle compared to surfaces without a nanocoating. The filtration mechanism was assessed by means of Porous Disk Filtration Analysis (PoDFA) and Liquid Metal Cleanliness Analyzer (LiMCA) monitoring systems, as well as by analysis of the used and infiltrated filters using Scanning Electron Microscopy and Energy Dispersive X-ray analysis (SEM/EDX) technology. Both short-term and long-term filtration trials showed that the filtration behaviors of the reference and nanocoated filters were comparable. It was therefore determined that nanocoating of such filters with Al₂O₃ does not provide any improvement with regard to filtration performance.

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I. INTRODUCTION

THE filtration of aluminum melts using ceramic foam filters is a state-of-the-art technology, with the efficiency of such filtration techniques influenced by a wide range of parameters that may be broadly divided into filter, inclusion, and process parameters.^[1] The knowledge on the mode of action of metal melt filters,

particularly the effect of wettability, surface energy, flow behavior of inclusions, grain refiner, *etc.*, is rather limited up to now. Therefore, the Collaborative Research Center 920 Multi-Functional Filters for Metal Melt Filtration—A Contribution towards Zero Defect Materials pursues to research the processes of metal melt filtration from several perspectives on a scientific basis.

There are two prevailing divergent opinions concerning the influence of the wetting behavior on the filtration. Bao *et al.*^[2,3] assume that improved wetting (*i.e.*, a lower contact angle) results in enhanced convergence of the aluminum melt with the filter surface, which increases the probability of a collision between inclusions and the filter wall. This theory, however, is limited to the measurement of filtration efficiencies and contact angles of the typical filter materials SiC and Al₂O₃. Filtration trials carried out using a Liquid Metal Cleanliness Analyzer (LiMCA) with SiC and Al₂O₃ filters and conducted at SAPA Heat Transfer (Finspång, Sweden) showed higher filtration efficiencies for SiC filters.^[4] The contact angles were evaluated using the sessile drop technique (contact heating) at 1000 °C,

CLAUDIA VOIGT, ENRICO STORTI, and CHRISTOS G. ANEZIRIS are with the Institute of Ceramic, Glass and Construction Materials, Technische Universität Bergakademie Freiberg, Agricolastr. 17, 09599 Freiberg, Germany. Contact e-mail: Claudia.voigt@ikgb.tu-freiberg.de BEATE FANKHÄNEL and MICHAEL STELTER are with the Institute for Nonferrous Metallurgy and Purest Materials, Technische Universität Bergakademie Freiberg, Leipziger Straße 34, 09599 Freiberg, Germany. BJÖRN DIETRICH and GOTTHARD WOLF are with the Department of Foundry Technology, Technische Universität Bergakademie Freiberg, Bernhard-von-Cotta-Straße 4, 09599 Freiberg, Germany. MARK BADOWSKI and MARGARITA GORSHUNOVA are with the Hydro Aluminium Rolled Products GmbH, Georg-von-Boeselager-Str. 21, 53117 Bonn, Germany.

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1100 °C, 1200 °C, and 1300 °C, and were extrapolated to a temperature of 700 °C, with the latter temperature yielding values of 79 deg for SiC and 97 deg for Al₂O₃.^[3]

Voigt *et al.*^[5] evaluated the filtration efficiency of the aluminum alloy AlSi7Mg with four filter materials (Al₂O₃, MgAl₂O₄, 3Al₂O₃, 2SiO₂, and TiO₂) with LiMCA measuring devices at a pilot filtration line at Constellium in France,^[6] whereby the contact angles at 730 °C were measured with a sessile drop testing apparatus equipped with a capillary purification unit. This temperature was selected due to ongoing reactions between the substrate and the aluminum when using higher temperatures of, *e.g.*, 950 °C.^[7] Comparison of the filtration efficiencies and contact angles measured showed a good correlation for inclusions smaller than 110 μm and the filtration efficiencies increased with increasing contact angle.

In contrast, Uemura *et al.*^[8] investigating the filtration of steel, used the equilibrium of forces for the calculation of the adhesive forces of inclusions at the filter wall and the determination of a relationship between the adhesive forces and the contact angle. The equation yields direct proportionality between the filtration effect and the contact angle, *i.e.*, the higher the contact angle the better the filtration effect. The filtration experiments of Uemura *et al.*^[8] with filters made of ZrO₂·Al₂O₃, ZrO₂, CaO·6Al₂O₃, and 3Al₂O₃·2SiO₂ did show any influence of the contact angle on the filtration efficiency. Uemura *et al.*^[8] assigned the small variations of the contact angles of the used filter materials as the reason.

However, the contact angle between aluminum and ceramic substrate depends on both the substrate material (chemistry and phase composition) and the roughness of the substrate's surface, which raises the question of which characteristic results in the greatest impact.

The application of nanofunctionalized coatings would result in an increase in the contact angle by increasing the surface energy without significantly changing the filter surface roughness.

In this work, the contact angle between the aluminum melt and the substrates with and without nanofunctionalization was determined by means of the sessile drop technique. Afterwards, alumina filters with and without nanofunctionalized surfaces were tested in short-term and long-term aluminum filtration trials to determine their filtration behavior.

For the determination of the wetting behavior between metal melts and solids, the sessile drop technique is preferred due to the simplicity of the experimental setup and the relatively convenient heating process. In this method, a test sample of metal is placed on the substrate, which is then introduced into a furnace. During the heating process and the dwell time, the shape of the drop is evaluated to determine the contact angles.^[9,10]

For the determination of filter behavior, LiMCA and PoDFA techniques are used, with the LiMCA monitoring system considered to be the reference technology for quantifying inclusions in molten aluminum.^[11] Based on the principle of the Coulter counter, LiMCA quantifies the inclusion number and size in molten aluminum.

PoDFA is a method for the metallographic observation of inclusions in aluminum, whereby liquid aluminum is pressed through a finely meshed filter and the inclusions are concentrated in the filter cake.^[11] PoDFA then evaluates the number, size, structure, and phase composition of the inclusions in the aluminum.

A basic requirement for the determination of the impact of nanofunctionalized surfaces is a comparable filter macro- and microstructure and functional pore size. This requirement was met by testing pre-sintered skeleton foams coated with an Al₂O₃ nanocoating alongside Al₂O₃ reference filters. For the manufacture of ceramic foam filters, the 'replica technique' by Schwartzwalder is an established process^[12] and involves using a polymeric foam which is coated with a ceramic slurry. After drying, the polymer is burned out and the ceramic material is sintered, generating a replica of the original polymeric foam structure.^[12]

II. MATERIALS AND METHODS

A. Preparation and Characterization of the Ceramic Foams and Substrates

For the proposed investigations, two kinds of samples were needed—substrates for contact angle measurements and ceramic foams filters for filtration trials with and without nanofunctionalization. Two different Al₂O₃ nanopowders were tested:

- Al₂O₃ nanosheets (100 pct α-Al₂O₃, length/width 0.5 to 3.0 μm), see Figure 1(a)),
- Al₂O₃ nanopowder (α-Al₂O₃, d₅₀ = 80 nm), see Figure 1(b)).

A slurry was then prepared for the filters coated with Al₂O₃ nanosheets (Sawyer) in which 0.4 g of Xanthan gum (Erbslöh, Germany) and 0.1 g of Dolapix CE64 (Zschimmer & Schwarz, Germany) were first dispersed in 100 ml of deionized water. In the next step, 1 g of alumina nanosheets was added and the suspension was sonicated by means of an ultrasonic homogenizer (Sonopuls HD 2200, 20 KHz, 200 W) for 3 minutes at 50 pct amplitude. Finally, 19 g of Martoxid MR70 alumina powder (Martinswerk, Germany) was slowly added while the slurry was stirred mechanically. The slurry produced was cold-sprayed onto pre-sintered 20 ppi alumina filters by means of an airgun Krautzberger HS-25HVPL, nozzle diameter: 2 mm, air pressure of 3 bar in a spraying chamber. Approximately 12 g of the slurry was deposited on each filter sample. After drying the filters at room temperature for 24 h, the filters were heated with a rate of 2 K/min to 1200 °C for 1 h and cooled down to room temperature without additional cooling.

For the preparation of the filters coated with Al₂O₃ nanopowder (IoLiTec Ionic Liquids Technologies GmbH), a slurry with a solid content of 9 wt pct was prepared with Al₂O₃ nanopowder, deionized water, and additives (in proportion to the quantity of Al₂O₃ nanopowder in the slurry). The additives used were 0.5 wt pct Optapix AC 170 (Zschimmer & Schwarz,

Fig. 1—SEM images of the Al_2O_3 nano powders (a) Al_2O_3 nanosheets and (b) Al_2O_3 nanopowder.

Germany), 0.3 wt pct Dolapix CE64, and 1.3 wt pct Xanthan gum (Erbslöh, Germany). The slurry was mixed in a ball mill (plastic bottle with alumina balls with a filling level of 50 vol pct) for 24 h and sonicated with an ultrasonic homogenizer (Sonopuls HD 2200, 20 KHz, 200 W) for 3 minutes at 50 pct amplitude, *i.e.*, with a power of 100 Hz. This slurry was used to coat pre-sintered Al_2O_3 filter skeletons and sintered Al_2O_3 substrates using a combined dip and centrifugation step, which employed a centrifuge immediately after dipping to remove excess slurry. At the end of the preparation process, the filters and substrates were sintered with the following sintering regime: The samples were heated up to 600 °C at a rate of 1 K/min, and then to the sintering temperature at a rate of 2 K/min with a holding time of 1 h and cooled down to room temperature without additional cooling.

Three different sintering temperatures were tested: 800 °C, 1250 °C, and 1600 °C.

A moderate impingement test was carried out to test the stability of the Al_2O_3 nanocoating on the filters during casting. The test equipment consisted of a sodium silicate-bonded pouring basin on top of a metal frame. The filter was fixed at the bottom of the pouring basin with regular core adhesive. Each filter was tested with 3 kg of molten aluminum alloy with 7 wt pct Si and 0.3 wt pct Mg according to European standard EN AC- AlSi7Mg0.3 (Trimet Aluminium AG, Germany), whereby the aluminum flowed through the filter without solidifying in it. The drop height of the liquid aluminum was approx. 30 cm. The pouring temperature was set at 730 °C, which was slightly higher than the normal pouring temperature for this alloy. Before and after the moderate impingement test, the nanocoated filters were evaluated by means of a Philips XL 30 scanning electron microscope (Philips, Germany).

B. Measurement of the Contact Angle

The sessile drop apparatus consisted of a high-temperature furnace with a high vacuum and an inert gas system from Carbolite Gero GmbH (Neuhausen, Germany). The image acquisition was carried out by means of a digital image analyzer. The AlSi7Mg aluminum alloy used was purchased from Trimet Aluminium AG

(Essen, Germany). Directly before placing the metal samples (with a mass of 60 ± 2 mg) on the substrate, the metal was cut to achieve surfaces with oxide layers thinner than 25 Å, as described by Bianconi *et al.*^[13]

The contact angle experiments all followed the same heating procedure. The furnace was first evacuated for 90 minutes to reach a pressure of $p \leq 1.5 \times 10^{-5}$ mbar. In the next step, the heating process commenced with a heating rate of 350 °C/h to a temperature of 950 °C, followed by a holding time of 180 minutes. After 180 minutes, an average pressure of $7.4 \pm 0.4 \times 10^{-6}$ mbar was measured within the furnace. At least two experiments were performed per sample type.

For small droplets ($m < 100$ mg), the contact angle can be calculated by assuming that the drop is a spherical segment. Consequently, the equation for calculating the contact angle from the measured height h and diameter d of the drop base is given in Eq. [1]^[14]:

$$\theta_s = 2 \arctan 2h/d \quad [1]$$

The height h and the diameter d of the droplets were taken from the digital images of the droplets.

The surface roughness of the substrates was measured in advance with the help of a VK-X laser scanning microscope (Keyence, Japan), whereby an area of $1500 \times 1400 \mu\text{m}^2$ in the center of the substrate was evaluated at a magnification of $\times 20$. The determination of the surface roughness S_a was conducted on processed areas such that the waviness was removed, whereby a cut-off wavelength λ_c of 2.5 was used. Each sample type was scanned at least 3 times.

C. Short-Term Filtration Trial

The short-term filtration trials were conducted at the metal foundry of Georg Herrmann Metallgiesserei GmbH (Germany) with AlSi7Mg (EN AC-42100) from Rheinfelden Alloys (Germany).

The presence of non-metallic inclusions is necessary for testing filters in terms of their filtration efficiency. Preliminary tests showed that the application of scrap material (recycled aluminum consisting of solidified feeders and runners) was a practicable way to introduce oxide films and non-metallic particles. A mixture of

50 wt pct ingots and 50 wt pct scrap was used for the filtration trials. The aluminum alloy (300 kg) was melted in an electrically heated furnace and skimmed directly before the casting process. No grain refinement was carried out but due to the use of scrap, grain refiner was introduced to the melt. Casting was performed at a melt temperature of 740 °C in a combined steel and green sand mold (see Figure 2), which was suitable for the testing of four different filters at the same time with comparable melt quality. In this study, only the results of the Al₂O₃ reference filter and the nanocoated Al₂O₃ filter are presented. The advantage of the experimental setup was the use of a single melt charge and a joint sprue, which resulted in excellent comparability with respect to the incoming particle load. The vertical sample mold and feeder were made of 42CrMo (mold diameter: 60 mm; mold height 165 mm) and coated with a commercial zircon coating. The joint vertical sprue and the horizontal runners were formed with green sand, see Figure 1. Two filters with a size of 50 × 50 × 22 mm³ and 20 ppi (pores per inch) were tested:

- An Al₂O₃ reference filter;
- An Al₂O₃ nanocoated filter (800 °C).

After casting and solidification of the aluminum alloy, the filters and the castings were extracted. The castings were analyzed by means of PoDFA analysis conducted by HOESCH Metallurgical Service (Germany). The cast filters were cut to a size of 6 mm in height and 25 mm in diameter, and embedded in epoxy resin. After hardening of the resin, the samples were ground and polished. The prepared samples were investigated using a Philips XL 30 SEM (Philips, Germany) equipped with an energy-dispersive X-ray spectroscopy device (Phoenix).

D. Long-Term Filtration Trials

The long-term filtration trials were performed at Hydro Aluminium Rolled Products GmbH (Germany) using filters with 30 ppi and a truncated pyramid shape with a square section of 145 mm × 145 mm on the

small side (melt outlet), 176 mm × 176 mm on the large section (melt inlet), and a thickness of 45 mm as prepared by the replica technique.

Two different filters were tested:

- An Al₂O₃ reference filter;
- An Al₂O₃ nanocoated filter (800 °C).

The lateral surfaces were covered with a gasket which expanded under the influence of the heat, ensuring that the melt passed through the entire height of the filter.

The schematic overview of the pilot filtration line used for the long-term trials is shown in Figure 3 and consists of a 1.5 t gas-fired melting furnace with three chambers, a launder system, a filter box, and a lifting pump. For the filtration experiments of the two different filters, 1.3 t of aluminum (wrought Al99.5 aluminum alloy ingots) were melted in the main chamber of the furnace and the dross was removed manually. During the trials, the aluminum melt was pumped into the elevated launder system with a small cascade upstream from the filter box. The aluminum melt passed the filter and flowed in a cascade back to the melting furnace, so that the aluminum melt was continuously pumped in a loop. No artificial inclusions were added for these experiments. The inclusions measured were either introduced by the material source, the melting process or the two cascades in the filtration loop.

The system was equipped with K-type thermocouples at the filter bowl, the main chamber and the pump chamber, an Alscan unit (ALSCAN 3, ABB Ltd., Canada), and two LiMCA II units (ABB Ltd., Canada), which facilitated continuous monitoring of both inclusion number and size in front of and behind the filter.

The filter box, the filter, and the launder system were preheated with a hot air burner before starting the loop. In the next step, the thermocouples, the Alscan unit, and the LiMCA devices were installed, after which the measurement was started and operated continuously for at least 45 minutes. Afterwards, 1.25 kg of AlTi3B1 grain refiner (AMG, UK) was added to the melt at a ratio of approximately 1 kg/t of aluminum, and a second monitoring sequence was conducted before the

Fig. 2—Casting system for the short-term filtration trials.

Fig. 3—Schematic overview of the filtration pilot line.

process was stopped. The filter was carefully removed from the filter box during the shutdown process in order to facilitate the solidification of the remaining aluminum and inclusions inside the filter plate.

For the subsequent sequence, the launder system was cleaned, set up, coated, and, after several hours of waiting time, the next filter was inserted and the next trial commenced with the preheating process, which was followed by the testing procedure described above.

III. RESULTS

A. Sample Characterization and Moderate Impingement Test

The nanocoated and sintered filters were evaluated with SEM (see Figure 4). The filter coated with Al_2O_3 nanosheets exhibited super-fine structures on the filter surface (Figure 4(a)).

At higher magnifications than the $\times 3000$ used for the SEM images in Figure 4, elongated, thin structures induced by the nanosheets used were visible. However, a magnification of $\times 3000$ was chosen to facilitate better comparability between the different filter types. After the moderate impingement test, these super-fine features disappeared and only the typical Al_2O_3 surface was visible with grains sizes ranging from approximately 2 to 10 μm (see Figure 5(a)). There were two possible explanations for this observation. One was that the nanosheet coating was washed off the filters by the aluminum melt due to insufficient bonding of the coating, while the other was that the nanosheets were

dissolved at 740 $^{\circ}\text{C}$ in the aluminum melt due to their reactivity. In summary, the nanosheet coating was not stable during the aluminum filtration process and, consequently, no further experiments with nanosheets were performed within the framework of this study.

Almost spherical super-fine particles (with diameters smaller than 1 μm) were observed on the nanopowder-coated filters sintered at 800 $^{\circ}\text{C}$ and 1250 $^{\circ}\text{C}$ (see Figures 4(b)) and (c)), whereas the filter sintered at 1600 $^{\circ}\text{C}$ exhibited significantly larger grains as the nanosized grains sintered together to form larger grains due to the high specific surface area and, hence, high reactivity. The nanopowder coating sintered at 800 $^{\circ}\text{C}$ and 1250 $^{\circ}\text{C}$ was still observable after the moderate impingement test and, therefore, the nanocoated filters sintered at 800 $^{\circ}\text{C}$ were chosen for both the short-term and long-term filtration trials.

B. Measurement of the Contact Angle

The influence of the surface roughness on the contact angle is described by Wenzel *et al.*,^[15] where an increase in the contact angle with increasing roughness is postulated for non-wetting systems (contact angle $> 90^{\circ}$) and a decrease in the contact angle with increasing roughness for wetting systems (contact angle $< 90^{\circ}$). Therefore, determination of the surface roughness is necessary for the evaluation of the contact angle. The three nanocoated substrates exhibited comparable surface roughness values S_a of between 2.2 and 2.5 μm (see Table I). The surface roughness of the Al_2O_3 reference substrate was slightly higher, at 2.9 μm .

Fig. 4—SEM images of the nanocoated filters with (a) nanosheets; (b) nanopowder sintered at 800 $^{\circ}\text{C}$; (c) nanopowder sintered at 1250 $^{\circ}\text{C}$; and (d) nanopowder sintered at 1600 $^{\circ}\text{C}$.

Fig. 5—SEM images of the nanocoated filters after the moderate impingement test: (a) nanosheets, (b) nanopowder sintered at 800 °C, and (c) nanopowder sintered at 1250 °C.

The contact angle measurements in the contact heating mode under vacuum exhibited a typical curve progression (see Figure 6). When the sessile drop apparatus reached the measuring temperature of 950 °C, the contact angle measurement commenced and indicated a high contact angle of 140 deg and higher. The contact angle then started to decrease, indicating the decomposition of the oxide skin on the aluminum.

After approximately 60 minutes, the decrease in the contact angle slowed down. A stable limit value was not reached within 180 minutes for the nanocoated substrates, but the contact angle changes were small after 120 minutes. Therefore, the contact angles were recorded after 180 minutes and listed in Table I. The repeated measurements correlated well with each other.

The nanocoated substrates sintered at 800 °C and 1250 °C exhibited a comparable contact angles of 124 and 125 deg, whereas the contact angle of the nanocoated substrate (which was sintered at 1600 °C) was much lower at 111 deg, though it was still higher than the 99 deg measured for the Al_2O_3 reference substrate. Based on the results of the surface roughness measurements (Table I), the roughness could be excluded as an influencing factor for the variation in the degree of wetting. The higher contact angles of the nanocoated materials sintered at 800 °C and 1250 °C were caused by the higher surface energy due to the high specific surface area of the Al_2O_3 nanocoating. The lower contact angle of the nanocoated substrate sintered at 1600 °C was due to the increased grain size of the nanocoating materials and, therefore, their lower specific surface area. The results correlated very well with the SEM analyses and revealed fine particles on the filter surfaces sintered at 800 °C and 1250 °C, whereas the nanocoating sintered at 1600 °C possessed larger grains.

For clarity reasons, the authors would like to differ between the apparent contact angle (contact angle on a real surface—rough and chemical heterogeneous surface) and the intrinsic contact angle (contact angle on an ideal surface—smooth, rigid, chemically homogeneous, insoluble, and non-reactive).^[16] Under the indicated conditions, the intrinsic contact angle depends on the chemistry, the phase composition, and the surface energy of a tested substrate and can be calculated by the Young's Equation

$$\cos \theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$$

whereby θ is the contact angle, γ_{sg} the surface free energy between solid and liquid, γ_{sl} the interfacial tension between solid and liquid, and γ_{lg} the surface tension between liquid and gas. In this study, the surface energy was varied by using nanosized coating in comparison to a reference material to vary the contact angle without changing the roughness, the chemical and the phase composition.

C. Short-Term Filtration Trial

Video recording of the filtration trial showed that all four feeders were filled equally within 16 seconds, thus indicating comparable filter flow rates. The non-metallic inclusions detected by SEM/EDX analysis of the tested and infiltrated filters were oxide films and particles (non-metallic inclusions), and consisted mainly of Al, Si, O, and Mg. It should be mentioned that the determination of the inclusion composition by EDX was difficult due to the small size of the inclusions and the different depths of the stimuli. For this reason, no statement on the inclusion chemistry could be made based on the SEM/EDX analysis. An area of 3 mm × 2.3 mm was investigated at the filter inlet and outlet on the tested and infiltrated filters by SEM in the back-scattered electron mode. The chosen area was scanned with a magnification of at least × 200. The number of inclusions found in the two tested filters was comparable.

The results of the PoDFA analysis of the two castings are shown in Table II, and show that Al_2O_3 films, carbides, magnesium oxide, spinel, refractory material, iron and manganese oxides, and grain refiners were detected in the castings. Generally, the higher the PoDFA index in mm^2 of inclusions per kilogram of aluminum tested, the higher is the impurity of the aluminum. A comparison of the two castings showed the lower PoDFA index value for the Al_2O_3 reference filter due to lower values for spinel or spinel-related inclusions. For the other inclusions types, the amounts detected for the two filters tested were comparable. According to the PoDFA analysis, the nanocoating did

Table I. Results of Surface Roughness and Contact Angle Measurements

	Nano 800 °C	Nano 1250 °C	Nano 1600 °C	Al ₂ O ₃ Reference 1600 °C
Surface Roughness S _a /μm	2.5 ± 0.1	2.4 ± 0.1	2.2 ± 0.1	2.9 ± 0.1
Contact Angle 1/deg	122	125	112	102
Contact Angle 2/deg	125	124	110	99
Average Contact Angle/deg	124 ± 2	125 ± 1	111 ± 1	101 ± 2

Fig. 6—Time dependency of the contact angle measured by sessile drop measurement.

not result in improved filtration. The experimental setup was accompanied by the following scientific disadvantages:

- Transient filtration performance due to the short trial period;
- Stochastic distribution of the aluminum melt, although a joint sprue was used;
- Compared to the standard hot PoDFA procedure, the cold PoDFA procedure applied bore the risk of particle removal or of the nature of the particles changing during the additional solidification and remelting step;
- Random position of the microsection for the PoDFA analysis and a 2D view on a 3D sample.

To confirm the results of the short-term filtration trial, additional long-term filtration trials were performed.

D. Long-Term Filtration Trials

The long-term filtration trials took place at a pilot filtration plant at Hydro Aluminium Rolled Products GmbH (Germany), and were divided into two parts: before and after the addition of 1.25 kg of AlTi3B1

grain refiner. The grain refiner TiB₂ was added as AlTi3B1 to enhance the dissolution and the formation of a fine, uniform aluminum grain structure.

In the period before the addition of the grain refiner, the effect of the filter was clearly recognizable in the LiMCA data by virtue of the high N20 value in front of the filter and the significantly reduced value behind the filter (see Figures 7 and 8). The reference filter and the nanofilter sintered at 800 °C exhibited comparable filtration behavior regarding the LiMCA results. The mean N20 LiMCA indexes (number of inclusions with a size between 20 and 300 μm in thousand inclusions per kilogram aluminum) in front of the reference filter and the nanofilter sintered at 800 °C were approx. 6.9 k/kg and 9.1 k/kg, respectively (see Table III). Behind the filter, the mean N20 LiMCA indexes were 0.20 k/kg (reference filter) and 0.23 k/kg (nanofilter at 800 °C), with mean filtration efficiencies (calculated with LiMCA N20 values) of 97.0 pct (Al₂O₃ reference) and 97.5 pct (nanofilter), as can be seen in Table III. Hence, no improvement in the filtration effect was detectable due to the nanocoating, a finding consistent with the results of the short-term filtration trials.

As mentioned in the literature,^[17,18] the addition of the AlTi3B1 grain refiner decreased the filtration efficiency, in that the AlTi3B1 decreased the N20 level in front of the filter and increased the N20 level behind the filter.^[17] The similar observations were found in this study, where the Al₂O₃ reference filter exhibited approximately stable behavior in contrast to the Al₂O₃ 800 °C nanofilter, which exhibited a decrease in the N20 value both in front of and behind the filter (see Figures 7 and 8).

For this reason, the mean N20 values for the nanocoated filter sintered at 800 °C had to be interpreted with caution (see Table III). Despite unstable N20 values, the results were obvious—the filtration efficiency decreased dramatically.

According to Laé *et al.*,^[19] the addition of grain refinement is assumed to prevent the formation of bridges in the filter consisting of non-metallic inclusions and to reduce the filtration rate. But there is no explanation for possible causes and no explanation for the decreasing N20 value in front of the filter. To the best of our knowledge, there are no scientific publications dealing with the effect of grain refiner on the filtration. The particle size of the refiner was in the range between 0.5 and 5 μm^[20], *i.e.*, relatively low compared to the non-metallic

Table II. Results of the PoDFA Analysis of the Short-Term Filtration Trial

Inclusion Types	Al ₂ O ₃ Reference Sintered at 1600 °C	Al ₂ O ₃ Nanocoating Sintered at 800 °C
Al ₂ O ₃ Films/Number Per kg	187 (length < 500 μm, thickness < 3 μm)	156 (length < 500 μm, thickness < 3 μm)
Carbides/mm ² kg ⁻¹	0.006	0.006
Magnesium Oxide/mm ² kg ⁻¹	0.004	0.004
Spinel/mm ² kg ⁻¹	0.198	0.333
Reacted Refractory Material (Spinel Related)/mm ² kg ⁻¹	0.015	0.048
Non-Reacted Refractory Material (α-Al ₂ O ₃ , CaO, SiO ₂ ...)/mm ² kg ⁻¹	0.009	—
Iron and Manganese Oxides/mm ² kg ⁻¹	0.005	0.008
Grain Refiner TiB ₂ /mm ² kg ⁻¹	0.009	—
Sum With/Without Grain Refiner/mm ² kg ⁻¹	0.245/0.236	0.399/0.399

Fig. 7—N20 LiMCA indexes from the long-term filtration trials for the Al₂O₃ reference filter.

inclusions discussed in this work. Additionally, in contrast to the non-metallic inclusions, the grain refiner particles are particularly good wetted by the aluminum.

SEM images (Figure 9) revealed small particles of the grain refiner in close proximity to the Al- and O-based inclusions, which might have resulted in the change in the filtration behavior. It would be conceivable that such docking of the grain refiner particles at the inclusions increases the density and leads to an enhanced settling of the inclusions. In order to confirm this theory, further filtration trials are necessary.

In a next step, the mean inclusion size was calculated and plotted in Figure 10. The mean inclusion size was comparable for the Al₂O₃ reference filter and the nanocoated filter at 800 °C. The mean inclusion size was the same both in front of and behind the filter, and only the scatter was larger behind the filter due to the lower number of inclusions. For the Al₂O₃ reference

Fig. 8—N20 LiMCA indexes of the long-term filtration trials for the nanocoated filter sintered at 800 °C.

filter, it was obvious that the mean inclusion size decreased from approx. 31 μm to approx. 25 μm after the addition of the AlTi3B1 grain refiner.

The PoDFA (Table IV) analysis found only two different kinds of inclusions: Aluminum oxide and grain refiner due to the Al99.5 wrought aluminum alloy used. The surprisingly high number of inclusions in front of the filter for the nanofilter at 800 °C cannot be currently explained. SEM analysis of the filter used also detected only Al- and O-based inclusions and grain refiner (see Figure 9), confirming the results of the PoDFA analysis.

IV. CONCLUSIONS

In this study, the filtration behavior of nano functionalized alumina filters was compared with alumina reference filters. Both filter types consisted of alumina and exhibited comparable surface roughness values and filter cell sizes. Additionally, sessile drop measurements showed differences in the contact angles between the

Table III. Mean N20 LiMCA Index

Filter	Mean N20 LiMCA Index/k/kg		Filtration Efficiency (Calculated from the Mean N20 LiMCA Index)/Pct
	In Front of Filter	Behind Filter	
Before Addition of AlTi3B1			
Reference Filter-1600 °C	6.86	0.20	97.0
Nanofilter-800 °C	9.13	0.23	97.4
After Addition of AlTi3B1			
Reference Filter-1600 °C	2.07	1.05	49.4
Nanofilter-800 °C (Not Stable)	3.04	1.33	56.1

Fig. 9—SEM images of the filter used: (a) reference Al_2O_3 , and (b) Al_2O_3 nanofilter at 800 °C.

Fig. 10—Mean inclusion size during the long-term filtration trials as a function of time and the addition of grain refiner.

aluminum melt and the two different surfaces—the alumina reference and the alumina nanocoated substrates—whereby the contact angle depended strongly on the sintering temperature of the nanocoating due to the decrease in the specific surface area with increasing sintering temperature.

Both the short-term and the long-term filtration trials showed comparable filtration behaviors for the alumina reference filter and the nanocoated alumina filter. Therefore, the nanocoating of the filters did not provide any improvement regarding filtration. Given the similar

starting conditions (alumina material, comparable roughness, filter cell size, and experimental conditions), the results give a first indication that the measured contact angles (differences were caused by differences in the surface energy of nanocoated and reference material) between metal melt and filter material did not have a significant influence on the filtration behavior. These findings implicate that the correlation found in the study about measured apparent contact angles and their filtration behavior of Voigt *et al.*^[5] (an increasing apparent contact angle caused an improved filtration efficiency for inclusions smaller than 110 μm) was not caused by the changes in the intrinsic contact angle but by the different roughness of the materials. The influence of the filter roughness on the filtration behavior was proven by Voigt *et al.*^[21] Nevertheless, an explanation of the influence of the roughness on the filtration is rather difficult. The filter roughness might affect the flow behavior of the metal melt passing the filter but a flow simulation of nano-structured particles or filter roughness could not be realized yet. It is currently determined under what assumptions and constraints such flow simulations could be performed within the framework of the CRC 920.

The addition of AlTi3B1 grain refiner reduced the filtration efficiency by approximately half, whereby the AlTi3B1 decreased the N20 in front of the filter and increased the N20 level behind the filter. Furthermore, the mean inclusion size decreased after addition of the AlTi3B1 grain refiner from approx. 31 μm to approx. 25 μm .

Table IV. PoDFA Analysis of the Long-Term Filtration Trial

	Al ₂ O ₃ Reference		Al ₂ O ₃ Nanofilter at 800 °C	
	In Front of Filter	Behind Filter	In Front of Filter	Behind Filter
Before Addition of Grain Refiner				
Al Oxide/mm ² kg ⁻¹	0.012	0.001	0.036	0.007
Grain Refiner TiB ₂ /mm ² kg ⁻¹	0.001			
After Addition of Grain Refiner				
Al Oxide/mm ² kg ⁻¹	0.011	0.001	0.252	0.001
Grain Refiner TiB ₂ /mm ² kg ⁻¹	0.016	0.003	0.028	0.003
Hydrogen Content/ml/100g (Alscan)	0.43 to 0.63		0.35 to 0.39	

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