Atomic Force Microscopy Investigation of the In Situ-Formed Oxide Layer at the Interface of Al₂O₃–C/Steel Melt in Terms of Adhesion Force and Roughness in a Model System

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Herein, the in situ-formed layers on carbon-bonded alumina refractories immersed in liquid 42CrMo4 steel at 1650 °C are investigated with regard to their macro- and microroughness, wetting properties, as well as adhesive interactions. Colloidal probe (CP) atomic force microscopy (AFM) are used to describe the adhesion in a water-based model system. To take the interaction between melt and the in situ layer into account, the adhesive force is measured via drop probe AFM using a model system with mercury droplets. For poorly wetted in situ layer samples, adhesion forces increase with smaller hold times in the melt due to a less homogeneous layer and vice versa if only van der Waals forces act. In contrast, the influence of the immersion time in the melt and the lattice parameter of the crystals on the layer is of minor importance for melt droplet–layer adhesion.

1. Introduction

Ceramic foam filters are used in metal melt filtration to increase metal pureness by separation of inclusion particles like alumina or magnesia. These nonmetallic inclusions can considerably affect the mechanical properties of casting products; therefore, high filtration efficiencies are desirable. It has been observed previously that an in situ-formed oxide layer can be generated on ceramic filters based on MgO–C, Al₂O₃–C, and Al₂O₃–MgO–C after immersion in liquid steel.[1–4] Zienert et al. showed in their studies via thermodynamic calculations that alumina is dissolved in small quantities in liquid steel.[5] If carbon is present at the interface, dissolved oxygen will react and form carbon monoxide, whereby this gas phase also contains small amounts of Al₂O₃ suboxides. Together with an Al enrichment in the melt near the interface, these suboxides are deposited on the surface again and form the so-called in situ layer. Using Al₂O₃–C finger tests immersed in liquid 42CrMo4 steel at 1650 °C, it is demonstrated that a corundum layer forms first and subsequently a (Al, Fe, Mg, Mn)-containing spinel layer is formed on top of it, with a varying spinel chemistry depending on the oxygen content.[6] The results are shown in Table 1. In addition to the chemical composition of the in situ layer, Zienert et al.’s study also investigates the crystal morphologies, primarily of crystals near cracks, whereby it can be stated that the morphology of the crystals themselves is independent of oxygen content. In this publication, the samples from Zienert et al.’s study are again used but are estimated with regard to their surface roughness on the micro- and macroscale in the relevant size range for adhesive forces (inclusion particle–layer interactions) and contact angle measurements, whereby the influences of the hold time in the melt as well as the lattice parameters are investigated. Crystal structure, roughness, and chemism have an influence on the wetting behavior and the adhesive forces; however, due to the high roughness, it is currently not possible to predict the behavior via an adequate model. Therefore, the samples are investigated by AFM via colloidal probe (CP) and drop probe force spectroscopy to better estimate the influence of the layer as well as the change while immersed in steel melt during metal melt filtration. Furthermore, using the example of the in situ layer topography data, it is shown how to predict the adhesion force distribution for pure van der Waals interactions.

Water-based model systems are often used in experimental research of metal melt filtration, as currently available measuring devices often cannot withstand the high temperatures above 1600 °C, or properties such as opacity severely limit applicable measuring methods.[7–9] The results presented later on use the water-based model system already described in other
Table 1. Hold times in melt and lattice parameters of the investigated finger test samples with in situ layers from Zienert et al.\textsuperscript{[16]}

| Sample Name | Hold time in melt [min] | 1 min | 2 min, F1 | 2 min, F2 | 2 min, F3 | 2 min, F4 | 2 min, F5 | 2 min, F6 | 2 min, F7 | 3 min |
|-------------|-------------------------|-------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-------|
| Hold time in melt [min] | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 3 |
| Oxygen content [ppm] | 60 | 57 | 53 | 43 | 40 | 39 | 37 |
| Lattice parameter [Å] | 8.0622 | 8.0565 | 8.0464 | 8.0374 | 8.0202 | 8.0387 | 8.0427 |



studies\textsuperscript{[10,11]} whereby the same wetting conditions as in the real case were realized by means of silanization. This means in detail that some of the surfaces have been functionalized using a silane, creating a very thin fluoroalkyl layer (PTFE-like structure) on top of the samples. This results in contact angles of up to 105° on smooth surfaces. The change of original wetting properties is used to also account for additional effects, namely, the occurrence of small bubbles on the filter material surface and associated capillary interactions. The investigations can now be carried out under room-temperature conditions with the nonopaque model melt water.

Roughness parameters are known to be scale dependent,\textsuperscript{[12]} so that measurements on different scales often lead to significantly varying results. Roughness parameters according to DIN EN ISO 4287\textsuperscript{[11]} are often used to describe surface roughness, namely, $R_{\text{pmt}}$ (peak to valley distance), $R_{e}$ (ten-point height), $R_{s}$ (arithmetical mean height), and root mean square (rms) height, whereby the following applies (Equation (1)–(4)).

\begin{align*}
R_{\text{pmt}} & = \max (Z_{\text{peak}}) + \max (Z_{\text{valley}}) \\
Z_{e} & = \frac{1}{5} \sum_{i=1}^{5} (Z_{\text{peak}} + Z_{\text{valley}}) \\
Z_{s} & = \frac{1}{l_{\text{r}}} \int_{0}^{b} |Z(x)| \, dx \\
r\text{ms} & = \sqrt{\frac{1}{l_{\text{r}}} \int_{0}^{l_{\text{r}}} Z^{2}(x) \, dx}
\end{align*}

with evaluation length $l_{\text{r}}$ and height $Z$. These characteristic values determined on a macroscopic scale also serve to take into account larger pores, for example, as a result of stably seated CO bubbles after the dissolution/reprecipitation reaction. To detect this with a certain probability, the stylus method\textsuperscript{[14]} is used. With regard to the metal melt process and thus the deposition of small microparticles, the microroughness is of particular interest, here measured via high resolution atomic force microscopy.

The adhesive forces between inclusion particle and refractory surface, which typically occur in quite small surface regions, are therefore strongly influenced by the surface roughness (as well as surface chemistry). Such related phenomena can, for instance, drop sharply in the case of van der Waals forces. Numerous models exist in the literature for the calculation of van der Waals forces on rough surfaces, whereby the models were often fitted to the experimental data by changing the characteristic minimum distance between the interacting surfaces, which sometimes leads to unrealistic distance values.\textsuperscript{[15–17]} Also, many models are only designed for nanoscale roughness or are based on the Derjaguin approximation,\textsuperscript{[18]} so that, for example, multiple contact points between particle and the corresponding surface, which is in this case the in situ layer, are not considered. An alternative is to adapt the model according to Cooper et al.\textsuperscript{[19–20]}. Cooper et al. use artificially generated rough surfaces, put both virtually “into contact,” and calculate the individual distances and finally the van der Waals forces for each pair of pixels. The calculated forces for directly vertical opposite pixel pairs are then summed up to the total adhesion force. Cooper’s model is advantageous in that multiple contacts can be correctly taken into account without restrictions, as can be seen for the Derjaguin approximation. Unfortunately, he only uses artificially generated surfaces in his publication. For the investigation in this work, real high-resolution AFM topography scans of the interacting surfaces (particle and in situ layer) are used instead. For the calculation of the Hamaker constant between alumina particle and spinel in situ layer in water, optical data from Bergstr"om are used.\textsuperscript{[20]} The nonretarding Hamaker constant is determined according to the following equations\textsuperscript{[21]} (Equation (5)–(9)).

\begin{align*}
A_{H} & = -\frac{3}{2} k_{B} T \sum_{n=0}^{\infty} \int_{r_{n}}^{\infty} x \ln(1 - \Delta_{13} \Delta_{23} e^{-x}) \, dx \\
& \approx -\frac{3}{2} k_{B} T \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \left( \frac{\Delta_{13} \Delta_{23}}{s} \right)^{2} \\
r_{n} & = \frac{2 \xi_{\text{m}} \sqrt{\varepsilon_{3}}}{c} \\
\Delta_{jk} & = \frac{\varepsilon_{j} - \varepsilon_{k}}{\varepsilon_{j} + \varepsilon_{k}} \\
(i_{n}^{2}) & = 1 + \frac{B}{1 + \varepsilon_{n}^{2}} + \sum_{i=1}^{N} \frac{C_{i}}{1 + \left( \frac{2 \omega_{i}}{\xi_{n}} \right)^{2} + \frac{\omega_{i}^{2}}{\omega_{0}^{2}}} \\
\xi_{n} & = n \left( \frac{4 \pi^{2} k_{B} T}{h} \right)
\end{align*}

with Boltzmann’s constant $k_{B}$, temperature $T$, sum term $s$, running number $n$, distance $l$, frequency $\xi_{n}$, imaginary dielectric response function $e(i_{n}^{2})$, Plank’s constant $h$, optical properties like oscillator strength $B$, damping coefficient $g$, relaxation frequency $\omega_{0}$, and absorption strength $C$ for all terms $l$. In future work, it will be shown how the results differ when using a retardation Hamaker constant, but this would go too far at this point. The van der Waals force of two interacting plates with unit area (Equation (10)) is thus given by\textsuperscript{[22]}
\[ F_{vdW, \text{plate-plate}} = \frac{A_H}{6\pi \varepsilon L} \]  

(10)

In addition to van der Waals forces, another attractive force often acts on poorly wetted surfaces, the capillary force. As there is a high probability that incomplete wetting occurs, the small bubbles arise on the surfaces and finally capillary bridges form when the two surfaces are in contact\[23\] even though the number of studies on rough hydrophobic surfaces is low compared with smooth ones. There exist some studies, especially for metal melt filter materials, which indicate that the adhesion force also increases with increasing roughness, as a higher roughness leads to more, larger, and stable nano- and microscaled bubbles.\[24,25\] However, the tendencies cannot absolutely be generalized, as the occurrence, number, size, but also the stability of the bubbles depend on the measuring conditions, the chemistry of the sample, and also the type and form of the asperities and pores. There also seems to be an optimum roughness at which the highest adhesive forces are measured under poor wetting conditions. While in previous work nonreactive filter materials made of Al\(_2\)O\(_3\) or Al\(_2\)O\(_3\)–C with variable particle size distribution of the raw materials are investigated, the in situ layer consists of continuously grown spinel crystals with an alumina layer between the crystals and the Al\(_2\)O\(_3\)–C refractory sample. Doing force spectroscopy measurements, the occurrence of a snap-in, that is, a “jump into contact” of the CP cantilever onto the surface, can be taken as an indicator for capillary interactions with small pinned bubbles.\[26\] Capillary forces also occur between two surfaces that are wet by a liquid bridge. A special case is the drop probe method: For liquid metal capillary interactions, Escobar et al. show how small microsized mercury droplets can be attached to the cantilever instead of a CP and how to interpret the force spectroscopy data.\[27\]

Another property that is usually connected to adhesive interactions is wettability, which describes the tendency of a solid to form a common interface with a liquid that comes into contact with it.\[22\] The characteristic value to describe wetting is the material-specific contact angle, often measured via sessile drop measurements. Contact angle measurements, especially the application of Young’s equation for further calculations\[28\] are actually intended for chemically and morphologically homogeneous (smooth) surfaces. However, the filter material as well as the in situ-formed oxide layer are rough, so the apparent angle cannot be called a Young contact angle, and further calculations may contain systematic errors. Difficulties can arise in correctly detecting both contour and baseline of the droplet due to the sample roughness, which can lead to serious errors.\[29\] This study compares automated with manual detection of these parameters. Nevertheless, the apparent contact angle shows as well tendencies and allows reasonable estimation concerning the wetting behavior.

2. Results and Discussion

As already mentioned, the in situ layer samples examined here originate from the publication by Zienert et al.\[6\] and were formed on Al\(_2\)O\(_3\)–C refractory samples (so-called finger tests). Figure 1 (left) shows macroscopic and microscopic images of a finger test sample, especially the formed in situ layer after treatment in the 42CrMo4 steel melt. They show in their work that the layer only forms in the area of contact with the melt due to the reaction already described. In the slag zone area of the finger test, very fine, distributed steel droplets can be detected by light microscopy and also AFM, but crystallization of the in situ layer does not occur. For the AFM investigation, it was necessary to cut the samples in smaller parts. It became evident that the in situ
layer could be peeled off quite cleanly from the remaining Al₂O₃−C body under slight mechanical stress. From Zienert et al.’s study, it is known that the layer forms within a few seconds after contact with melt; however, the coverage of the Al₂O₃−C refractory surface only increases between 30 and 60 s and is “homogeneously” distributed on the surface after 2 min of being immersed in the steel melt. It is unclear whether the layer becomes denser or thicker; quantitative data are still lacking. The layer thicknesses of samples 2 min, F7 (lattice parameter 8.0427 Å), 2 min, F1 (8.0622 Å), and 3 min are therefore measured by scanning electron microscopy (SEM), whereby the layer of sample 2 min, F7 is shown as an example in Figure 1, top middle. The layer thicknesses here lie in between 20 and 25 μm and do not differ significantly for the three samples mentioned. In contrast, the layer is significantly thinner at a hold time of 1 min, namely, 7 and 10 μm.

SEM images, but especially AFM topography scans, show in detail the morphology of the formed crystals. The insets of the AFM scans show the corresponding error signal images with which edges can be sharply imaged. The two AFM scans in Figure 1, right, display hexagonal and triangular crystals, where edges can be sharply imaged. The two AFM scans in Figure 1, right, display hexagonal and triangular crystals, whereby the image sizes between 10 × 10 μm² and 2 × 2 μm² were chosen to be able to map complete crystals with high resolution. The crystals have heights of 500−1000 nm (triangular crystals) and 800−2000 nm (hexagonal crystals) and are thus smaller than the values given by Zienert et al., which were determined using a confocal laser microscope. The reason for this is, on the one hand, that crystal heights were mainly measured at cracks (whereby the height results from the crystal peak to ground level) and the laser-optical micrographs generate less precise values compared with AFM. In contrast, taking all AFM scans together, they investigate a significantly smaller number of crystals due to the much smaller total scan size, which leads to statistically less reliable values. The steps on the crystal surfaces determined by AFM amount to heights of 15−20 nm (triangular crystals) and 80−100 nm (hexagonal crystals), respectively. The detected nuclei (an example is shown on the triangular crystal in Figure 1) form on top of the crystal. Individual nuclei can grow together (in Figure 1, they have a height of about 45 nm), but are also surrounded by smaller nuclei (5−8 nm height). If the crystals of the in situ layer come into contact with inclusion particles during melt filtration, these structures alone can strongly influence the adhesive force.

Besides crystal growth itself, it is also interesting to see whether the porosity changes due to the growing in situ layer. Therefore, the in situ layer of sample 2 min, F7 was completely delaminated to provide sufficient material for the porosimetry measurement. The resulting pore size distribution is very widely distributed between 25 nm and 2 μm, with peaks at 29−58 nm and 1.4−2.7 μm. These pores lead to additional phenomena under poor wetting conditions, which will be discussed later on.

2.1. Wetting Properties of the In Situ Layer Samples

Sessile drop measurements are used to describe the wetting properties of the in situ layer surfaces that are investigated in the model system, on the one hand, to check the success of silanization and, on the other hand, to assess the influence of hold time and lattice parameter. It can be said in advance that in the case of good wettability, a suction of the liquid droplet, through the detected pores and, under poor wetting conditions, a formation of (nano-, micro-) bubbles become possible, which lead to strong deviations from the contact angle value of ideal surfaces (this is 105° for surfaces coated with Dynasylan)[109]. The determination of the contact angle is usually automated to keep the human influencing factor as low as possible. However, a precise determination of the baseline is difficult, investigating such
rough surfaces: in contrast to very smooth surfaces, the droplet is hardly reflected downward and the roughnesses close to the three-phase contact line can variably influence the illumination conditions, so that a globally set threshold leads to erroneous detection during binarization (see inset in Figure 2, top left). In contrast, manual baseline detection is time-consuming and not reproducible. Especially with high contact angles, deviations of just a few pixels can lead to massive errors. For this reason, a MatLAB script with automated baseline detection was compared with a device-specific LabVIEW script with manual baseline selection, both for the water contact angles on the hydrophobized samples (triangles: manual, crosses: automated). The two scripts use the circular approximation to determine the contact angle. There are also other possibilities for calculation such as elliptical and polynomial approximation or Young–Laplace curve fitting, but these are not considered for comparison purposes. Figure 2, top right, shows an example of a weak automated baseline fit (green line); here, the characteristic line is set too high due to the incorrect choice of binarization threshold. As the finger test samples differed slightly despite constant light and camera settings, the threshold must be varied a few percent for each sample to determine the baseline for all 20 droplets per sample. The comparison with the manually selected line shows that the results are very similar. What can be seen in the diagram in Figure 2 is that the water contact angle of the untreated in situ layer samples is lowest at the smallest holding time (1 min), 44°, as well as finger 2 min, F1 (first sample of 2 min test series, highest oxygen level), 68°, but still above the measured contact angle for the pure Al2O3–C finger. It could also be observed that some drops were sucked in after a few seconds on sample 2 min, F1, resulting in large error bars. From this, it can be concluded that the formed in situ layers on these finger test samples are very inhomogeneous. On the contrary, the other samples, 2 min, F2–F7, as well as 3 min, show quite similar mean contact angles with values ranging between 107° and 112°. This is somewhat unusual, as contact angle measurements with other filter materials made of alumina or spinel show contact angles below 90°, which is attributable to the in situ formation. After silanization of all samples, the mean contact angles show values between 130° and 135° independent of the hold time in the melt and the lattice parameter. The mercury contact angles lie slightly above this and fluctuate somewhat more (values are between 133° and 143°), but here no significant influence of a hold time can be detected, too. Note that the calculated confidence intervals, error bars, respectively, are very small (e.g., H2O silanized: 0.8°–1.8°, Hg untreated: 0.8°–2.5°, MatLAB H2O untreated: 1.2°–2.2°).

### 2.2. Roughness Parameters on Two Scales

In addition to wetting properties and chemism, roughness also plays an important role regarding adhesion forces between inclusion particles and in situ layer, as this is dependent on the contact area and distance to the latter. Therefore, Figure 3 shows the results of the determined roughness parameters of the in situ layer on two scales, whereby the stylus method is relevant for the evaluation of the contact angle measurements and contact-mode AFM results are used for the determination of the crystal sizes as well as for subsequent modeling. The ten-point heights and peak-to-valley distances are by definition higher than the values for Ra and rms roughness, respectively. What is recognizable for both scales is the scale dependence of the roughness parameters. It should therefore be pointed out again that an indication of the scale of the roughness measurement is essential for later model investigations, contact angle, and adhesive force measurements, but it is often insufficiently mentioned in the literature:

![Figure 3](image-url)
for example, in the Rabinovich model (calculation of van der Waals forces on rough surfaces), it is completely unclear on which scale the limitation refers and whether this is relevant for the contact areas of the interacting surfaces.\[17\] The results of the roughness determination on the macroscopic scale, including the error bars (5% significance level), show no clear correlation between lattice parameter/oxygen content of the melt and roughness. The values lie between 13.4 and 17.9 μm for \(R_z\) and 1.7 and 2.8 μm for \(R_a\) and rms. Nevertheless, the formation of the in situ layer leads to a strong roughening of the refractory surface: for the pure Al₂O₃/C refractory, the average value is \(R_z = 10.7 \, \mu m\). Even though rms and \(R_a\) are hardly different (\(R_z = 1.4 \, \mu m\) and rms = 1.8 μm for Al₂O₃–C refractory sample), an \(R_z\) difference of more than 7 μm is quite large, and it becomes clear that bubbles form during immersion with water or that these sites serve as placeholders for the CO bubbles during metal melt filtration. The difference between \(R_z\) and layer thickness makes clear that it is not possible for the stylus to reach the Al₂O₃–C body, either because the conical shape is broader than the pores or, also visible on the SEM image in Figure 1, there are crystals underneath. Thus, the CO bubble formation during hold time in the melt occurs staggered at locally adjacent points. The microroughness is determined using contact-mode AFM, whereby the roughness parameters of all scan lines are averaged from 3D datasets (Figure 3, bottom). It can be seen on the smaller scale too that there is no clear correlation between the lattice parameters of the spinel crystals and the common roughness parameters; the values for all 2 min-hold time samples range between 2.63 and 3.47 μm for \(R_{ptv}\), 0.50 and 0.64 μm for rms, and 0.39 and 0.52 μm for \(R_a\), respectively. The confidence intervals (error bars) in relation to the mean values are similar in magnitude to the results of the macroscale. This is surprising, as a higher scatter is usually expected due to the smaller scan size. Microroughness values of the pure Al₂O₃–C surface without in situ layer are instead lower at \(R_{ptv} = 1.347 \, \mu m\), \(R_a = 0.211 \, \mu m\), and \(rms = 0.26 \, \mu m\). This shows even more clearly on a smaller scale that the formation of the layer leads to a significant roughening of the surface. If the roughness values are plotted against the hold time, a slight increase with longer hold time can be observed for the average \(R_z\) and rms values, although the increase lies within the confidence intervals of the values. The \(R_{ptv}\) values fluctuate more strongly instead, so that no statement can be made for the ten-point heights. Nevertheless, the small increase in rms and \(R_a\), respectively, can influence the adhesive forces, which will be shown in the next chapter. However, as the rms values are well above the (not further described) limits of existing adhesion models given in literature,\[17\] the 3D raw data are used instead of calculated roughness parameters for subsequent modeling.

2.3. Force Spectroscopy Using Untreated In Situ Layers and Modeling

Force spectroscopic measurements are carried out with the method described by Ducker\[31\] and Butt,\[32\] whereby alumina particles with diameters between 25 and 34 μm are used (for exemplary image, see Figure 4).

To be able to compare the measurements with other results, the adhesive forces, calculated from force distance curves using a MatLAB script, are normalized to the particle radius. Adhesive forces on rough surfaces are distributed quantities,\[33\] as the
contact zones of the particle in situ layer differ at each point due to roughness but also due to chemical inhomogeneity (incomplete oxide layer, varying spinel lattice parameter) and are therefore shown cumulatively in the diagram in Figure 4 (bottom). The adhesive forces shown in the diagram represent measurements on untreated particles and layer surfaces. As no snap-in events were detected, it can be assumed that the attractive force is caused purely by van der Waals interactions between alumina—water—in situ layers. The diagram in Figure 4, bottom, shows very clearly that the measured adhesive force distribution for the Al₂O₃ particle on the pure Al₂O₃ finger without an in situ-formed layer is located further to the left compared with the force distributions of the in situ layer samples, that is, lower adhesive forces are measured on average; the median force, \( F/R_{50} \), calculates to 0.046 mN m⁻¹. Instead, the formation of the in situ layer leads to a shift of the adhesive force distributions toward larger values (\( F/R_{50} \) ranges from 0.161 to 0.283 mN m⁻¹). It can be seen that there are transition areas, which are expected due to the inhomogeneities mentioned earlier. Nevertheless, the characteristic median values \( F/R_{50} \) show that the adhesive force between particle and layer increases with increasing hold time in the melt. The experimental data show that a smaller lattice parameter or oxygen content in the melt leads to higher adhesive forces, that is, that chemism somewhat overcomes the effect of high roughness. However, it can also be seen that the adhesive force behaves significantly different with the smallest spinel lattice parameter, although the lowest roughness parameters were determined for this sample.

2.4. Force Spectroscopy Using Silanized In Situ Layers and CPs

Silanization of both surfaces ensures a similar wetting state, as can be seen for the interaction of sample surfaces with molten metal (see Figure 2). As shown in Figure 5, bottom, microbubbles partly appear visible by an optical microscope. They are strongly pinned within roughnesses and pores (see SEM image in Figure 1) and therefore do not have an ideally circular three-phase contact line. The formation of such strongly pinned microbubbles could already be observed on other filter materials with similar roughness parameters without an in situ layer. Here, too, the same microbubbles do not necessarily appear at the same pores and roughnesses during repeated immersion, but the amount of the surface area occupied by the microbubbles is much larger for sample 1 min than for the ones with longer hold time. If a CP particle hits one of these microbubbles, such large capillary forces arise after film breakage, where the full distance of the Z-scanner (10 μm) is not sufficient to let the particle detach from the refractory sample surface. In the case of capillary forces with such optically visible microbubbles, it can be said quite confidently on the basis of the results of Hoppach et al. that the inclusions remain trapped on the refractory materials during filtration because the flow-induced shear forces are not sufficient to redisperse them. Therefore, areas without microbubbles are of particular interest. An example of a force distance curve is shown in Figure 5, bottom: A slight repulsion occurs just before the snap-in, which has already been investigated by Ditscherlein et al. In the curve shown here, a less sharply formed pull off occurs, which indicates a deformation of the bubble until the particle snaps off. However, this only occurs with quite large attractive forces, that is, large capillary bridges. The cumulative adhesive forces in the diagram in Figure 5, top, are more broadly distributed compared with Figure 4, as two mechanisms act here as contributions to the total force. In contrast to the first system, just the opposite relationships arise for the hold times in the case of poorly wet in situ layer samples: With increasing hold time, the force distributions shift to the left toward smaller values, which is associated with a smaller amount of snap-in events. This can also be seen in the

![Figure 5.](image-url) Force spectroscopy results of the silanized in situ layer samples (top left), light microscopy image with observed microbubbles (bottom left), an exemplary force displacement curve (bottom middle), and correlations between snap-in events, oxygen content, and lattice parameter with median force (right).
amount of snap-in (ratio of snap-in events to total number of force distance curves) versus median value plot. With regard to the influence of the lattice parameter or oxygen content of the melt, a slight increase in the median force value with decreasing lattice parameter or oxygen content, respectively, is observable.

2.5. Force Spectroscopy with Drop Probe AFM

To simulate the interaction between the melt and the in situ layer, a small mercury droplet was attached onto the cantilever as model melt using Escobal’s method[27] instead of the CP. The adhesive forces were measured using the same procedure as for CP AFM. Due to the high roughness of the in situ layer and the large contact angle of mercury, the detected snap-in forces are rather small and lie between 6 nN and, quite rarely, 100 nN. It can therefore be assumed that during contact with the in situ layer, air cushions (micro- and nanobubbles) remain within the roughnesses and pores. As with the water-based model system, this is somewhat different from the real process, as the number of bubbles or air cushions should be larger under real conditions due to the formation of CO bubbles. Currently, this reaction cannot be realistically simulated in the model systems. The diagram in Figure 6, top, shows that the adhesive force distribution shapes differ only slightly from each other and are very close together. The median values increase slightly with higher hold time, from 5.7 mN m$^{-1}$ (1 min) to $= 6.9$ mN m$^{-1}$ (3 min), proportionally significantly less compared with the measurements using the water-based model systems (van der Waals forces and capillary interactions, see Figure 4 and 5).

This is why the diagram in Figure 6 only contains four measurement series, as there are hardly significant changes. If the microscopically determined median forces are plotted against the macroscopic contact angles, a simple correlation of the data is not precisely predictable due to the scatter. If pull-off distances are plotted against the measured adhesion forces, it can be seen that the larger the pull-off distance, the larger the measured force. It can therefore be assumed that the droplet is not completely pinned until it snaps off, as the retract curves would increasingly flatten due to droplet deformation. In fact, most of the trace and retract curves that were recorded show steps that indicate a three-phase line shift.

2.6. Discussion

Based on the thickness measurement, it can be deduced that the layer growth is degressive, as the mass transfer resistance increases. Together with the observation that intense gas bubbling near the refractory’s surface stops after 1 min treatment of the finger test samples in the melt from Zienert et al.’s work, it can be assumed that the reaction for formation of the in situ layer is almost complete.

Even with thinner layer thicknesses of 7–10 μm, it can be concluded that the underlying Al$_2$O$_3$–C refractory sample no longer has any influence on the van der Waals interactions. According to this, the deposition of the inclusion particles in the close vicinity of the filter surface depends on the properties of the in situ layer; thus, interactions with the initially formed alumina layer or the spinel crystals become effective, of which the second is more probable based on SEM and AFM images.

Figure 6. Exemplary mercury drop probe (top left) and force spectroscopy results for samples 1 min, 2 min F4, 2 min F5, and 3 min (top right), as well as correlation between pull off distance with adhesion force and median forces with mean contact angles (bottom).
The contact angle measurements of the untreated in situ layer samples clearly show that the layer is so inhomogeneous at hold times \( \leq 1 \) min or a lattice parameter of 8.0622 Å (i.e., the first 2 min sample at the highest oxygen content in the steel melt) that the water droplets are sucked in within a few seconds. This has measurable effects on the force measurements, namely, smaller median values. Interestingly, there are almost no differences between the other samples with lower lattice parameters or hold times of at least 2 min. If the median values of the adhesive force measurements are correlated with the averaged contact angles of the untreated samples, no relation can be seen, that is, the influence of roughness outweighs the influence of chemism on the size scale of contact angles. The macroroughness parameters relevant for the contact angle measurements do not show any relation concerning lattice parameters or longer hold times, which is why the contact angle results accordingly show no correlation. As already mentioned earlier, for the force measurement, roughness and chemism are relevant on smaller scales, which, however, vary depending on the size and shape of the inclusion particles. In the case of alumina particles in contact with spinel surfaces, the Derjaguin-Muller-Toporov contact mechanics model is applicable.[35] Using common Young’s moduli, adhesion energies, and the given particle size range, contact radii are in hundreds of nanometers and contact surfaces in tens of \( \text{nm}^2 \) range, which might be enlarged a bit if multiple contact points due to roughnesses occur. Taking into account the sizes of the crystals and aforementioned contact mechanics calculations, it is likely with the selected particle sizes relevant for metal melt filtration that they will either have contact with one crystal at axial impact or, in the case of pores, contacts with 2–3 crystals. The height of crystal steps, but also the nuclei, which seems to occur more frequently at lower hold times, significantly changes the adhesive force. For nucleation points with heights of 5–8 nm, van der Waals forces in the case of plate—plate interactions can theoretically drop to 0.2/1000 at worst (calculated with 0.3 nm minimum distance). However, this drop does not occur in the experimental tests (maximum difference of the median force values amounts to a factor of 10), which can be explained by the multiple contact points due to the roughness of both surfaces. A first rough estimation on the influence of microroughness on the measured normalized forces (pure van der Waals attraction) between alumina particle and in situ layer using the water-based model system is 0.0753\( \Delta \text{rms}^{-6} \). For more precise modeling purposes, the case of pure van der Waals interactions in the model system can be applied via a combination of the Cooper model and real topographies of the interacting surfaces. The extent to which lattice parameters or the \( \text{Al}_2\text{O}_3 \)–C body influences the measured forces cannot be sufficiently proofed theoretically, as there are no optical data in the literature for these different spinels or the finger test material after coking. To be able to estimate, at least roughly, whether the data fits the system alumina–water–spinel, a virtual force spectroscopy versus the experimental distribution of 2 min, F7 is shown in Figure 7. The optical data of cubic \( \text{MgAl}_2\text{O}_4 \) spinel and alpha–corundum are used.[20] For the nonretarding Hamaker constant, Equation (5)—(9) yield a value of \( \mathcal{A}_H = 2.971 \times 10^{-21} \text{J} \). Small scan sizes for particle and in situ layer sample surface with appropriate resolution are primarily used to minimize a calculation error due to surfaces that are too coarse. The topographies obtained by contact AFM are virtually moved toward each other until the minimum distance is reached on at least one point (pair of pixels). The van der Waals force of the pixel pairs (Equation (11)) as well as the total force (Equation (12)) is given by

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\mathcal{A}_H = \frac{2.971 \times 10^{-21}}{21} \text{J}
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According to Equation (11), the force drops very rapidly with distance, so that ultimately only very small zones are responsible for adhesion. As shown in Figure 7 (top), there can be single but also multiple contact zones that contribute to the adhesion force; the individual forces per pixel pair are finally added up. Due to the roughness of both surfaces, the multiple contact zones do not have to be directly next to each other. As the particle has a smaller scan size than the in situ layer, a virtual 2D mapping can be carried out as in the experiment. This cumulated data agree surprisingly well with the experimental one. The agreement depends on the quantitative roughness information from the AFM measurement of the substrate sample, which can be affected by the choice of the field of view.

In the case of silanized sample surfaces, smaller adhesive forces should actually be measured when considering only van der Waals interactions, as the Dyansylan structure is similar to PTFE. Nevertheless, larger adhesive forces are measured compared with the uncoated surfaces. If the pores serve as placeholders for stably seated bubbles under poor wetting conditions, capillary forces come into play and enlarge adhesive interactions by a factor of about 2 – 100 (samples 3 and 1 min). The pores in the micrometer range, as can also been seen in the SEM image and the porosity measurement, potentially lead to microbubble generation in case of incomplete immersion (in the real case CO bubbles, in the model system by hydrophobic surfaces). The nanoscale values arise from small pores between very closely spaced crystals; nanobubbles can sit stable here as it was observed in the study by Ditscherlein et al.[36] for oxide filter material. The force distance curves, or more precisely the snap in distances, can also be used to roughly estimate the heights of the bubbles. These lie between 13 and 400 nm, although some curves show distances up to 4 μm. Taking into account the measured peaks from mercury intrusion porosimetry measurement, the cap-shaped bubbles can grow significantly more out of the pore without being detached due to the surface inhomogeneity. With formation of a three-phase contact, larger adhesive forces can then be measured up to a certain degree: larger bubbles deform stronger until the particle breaks off. In the AFM experiments, an almost linear correlation of the adhesive force with pull-off distance could be demonstrated up to about 2 μm; maximum pull off distances are 3 μm. In this range, the attractive overall force fluctuates between 150 and 270 nN. Based on measurements on very smooth surfaces coated with Dynasylan, the water contact angle on the in situ layer is significantly higher (from 105° to 130° – 135°) and is due to bubble formation. This has been observed also for other filter material samples.[24]

In contrast to the untreated samples, the contact angle results of the silanized samples and measurements with Hg are not dependent on hold time and are also independent of the lattice parameter; thus, the additional occurrence of microbubbles leads to similar contact angles. The behavior is different with adhesive forces, where there is a trend related to hold time/microroughness and occurrence of snap ins, that is, nanobubbles. A rough approximation of the influence of microroughness on the measured normalized forces between alumina particle and in situ layer under poor wetting conditions using the water-based model system is 1.7705Δrms3.523.

The measured median forces from the water-based model system with coated surfaces can be compared with the results of the Hg droplet: by only looking at the median force values on both model systems, the values for the mercury droplet appear higher; in other words, the inclusion particle would either not adhere to the filter at all or detach again. However, capillary forces are linearly dependent on the surface tension of the liquid, which also applies to interactions with nanobubbles,[17,38] so that the adhesive forces have to be converted by a factor 0.0728 N m⁻¹ = 6.59. Therefore, the capillary interaction between particle, bubble, and in situ layer in the model melt significantly exceeds the interaction between melt and in situ layer. Regarding Hoppach et al.’s results, such adhesive interactions are large enough to overcome flow-induced shear forces. This means that the inclusion particle can still be separated in the melt despite the changed surface roughness due to the formation of the in situ layer, although a water-based model system is used for force measurements.

3. Conclusion

In this study, which serves as a continuation of Zienert et al.’s work,[6] the in situ-formed layer upon contact of the Al₂O₃—C finger with steel melt was investigated in terms of roughness, wettability, and adhesive interactions.

The wettability investigations showed that, except for water droplets on the untreated in situ layer with the lowest hold time in the melt, the mean contact angles are neither dependent on the hold time, nor on the spinel lattice parameter. This is caused by similar roughness parameters on the macroscale, which seems to be independent of the two mentioned varied parameters. Adhesive force measurements on the macroscale using a model system show instead that hold time and lattice parameters have an influence on adhesive forces between particle and in situ layer. In the case of pure van der Waals forces, a longer hold time leads to higher forces; if capillary forces act additionally as a result of pre-existing nanobubbles, this correlation is reversed because the layer is thinner and more inhomogeneous for shorter hold times. In both cases, the adhesive forces decrease with increasing lattice parameters, although less markedly compared with hold time. Even though no optical data for the different spinel crystals exist at the moment, the results of the simulated force spectroscopy using optical data of MgAl₂O₄ spinel as well as AFM topography scans and experimental results were in good accordance. Drop probe AFM measurements with mercury yielded values which, after conversion to same system conditions, show that inclusion particles can be stably attached on the in situ layer during melt filtration.

4. Experimental Section

Model System: Roughness investigations and drop probe—AFM measurements were done under dry conditions. For all other measurements, a water-based model system described in the study by Fritzschke et al.[10] was used for force spectroscopy investigations. To mimic the real
process of metal melt filtration and therefore include capillary interactions, the CP as well as the in situ layer samples were silanized with Dynasylan F8261 from Evonik, Germany, using the method described in the study by Heuzeroth.[13] Dynasylan F8261 was a fluoroalkyl functional silane that acted as a surface modifier on hydroxy functional substrates. To be able to carry out the contact angle and AFM measurements, the finger tests from Zienert et al.’s work were cut into 6 × 4 × 8 mm$^3$ samples, as the AFM liquid cell only had a limited volume and the entire finger should not be silanized for control samples.

**Contact Angle Measurement:** Contact angles of all pure and silanized finger test samples were measured using a self-build contact angle measuring device for sessile drop investigations. After image acquisition, a MatLAB script was used to calculate the contact angles using circle, ellipse, and Young–Laplace curve approximation. For each finger test, 15 droplets with a droplet volume of 3 μl were placed carefully on the in situ layer surface. MilliQ water and mercury from Carl Roth, Germany, were used for the measurements.

**Roughness Parameters via Hommel Tester T1000 from Jenoptik AG, Germany:** Macroscopic roughness parameters of the finger test samples were determined using the DIN EN ISO 11562 standard and mode M1 of the Hommel Tester. Here, a diamond tip scanned along a 1 cm line, detecting the height profile of the sample, and roughness parameters like $R_s$, $R_a$, and rms were calculated. For each finger test sample, 15 measurements took place along the length and width of the in situ layer to provide statistically robust data.

**Roughness Parameters via AFM XE-100 from Park Systems, South Korea:** The finger test samples were imaged by contact-mode atomic force microscopy using a standard contact-mode cantilever (ContAl-G from Budget Sensors, spring constant after calibration: 0.2 N m$^{-1}$). On 3–6 different locations on the in situ layer, 10 μm × 10 μm-sized images were recorded for each sample. A MatLAB script including sample drift correction and calculation of microscale roughness parameters like $R_{rvt}$, $R_s$ and rms was used.

**Mercury Intrusion Porosimetry via PASCAL 140/PASCAL 440 from Porotec GmbH, Germany:** The delaminated in situ layer was weighed and filled into the dilatometer. First, the measurement curve was recorded in the low-pressure range, where macro pores up to 58 μm were detected. Then, the dilatometer together with the sample was clamped into the high-pressure range, where macropores up to 58 μm were detected. A double determination was carried out using standard values for pore size calculation (mercury contact angle: 140° and mercury surface tension: 0.48 N m$^{-1}$).

**CP-AFM:** Force spectroscopy measurements were done using alumina CP cantilevers, as described in the study by Lohse et al.[24] For each finger test sample, force distance curves were recorded, that is, 256 curves in a 20 μm × 20 μm area on six different locations. This resulted in more than 1500 force distance curves per sample to ensure statistically robust data sets. For the uncoated system, cantilevers of type AIOAI-TL A (0.2 N m$^{-1}$) and for the silanized system AIOAI-TLB cantilevers (1.85 N m$^{-1}$) both cantilevers from Budget Sensors, Bulgaria) were used due to the different magnitudes of adhesion forces.

**Drop Probe-AFM (CP-AFM):** Drop probe measurements were done using the method described in detail by Escobar et al.[27] Small microsized mercury droplets were used as CPs on stiff cantilevers (AIOAI-TL C, 22.13 N m$^{-1}$). For four of the finger test samples, force spectroscopy measurements were realized on four different locations on each sample; each 2D map consisted of 256 force distance curves.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Data available on request from the authors.

**Keywords**

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