Immersion Testing of Variously Coated Ceramic Foam Filters in an AZ91 Magnesium Melt

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Herein, the aim is to investigate the applicability of various ceramic foam filter materials in the filtration of magnesium alloy melts. The durability of ceramic foam filters is studied throughout their immersion in an AZ91 melt for up to 60 min at 680 °C. The four selected types of ceramic foam samples consist of ZrO₂, uncoated Al₂O₃-C and Al₂O₃-C coated in MgAlON or Al₂O₃. Immersion tests are conducted for 5–60 min in a vertical tube furnace in an Ar/SF₆ protective atmosphere. After their immersion, the cooled filters are evaluated by means of optical and scanning electron microscopy (SEM). Every filter sample retrieved from the melt is intact; layers of MgO and occasional metal droplets are found on their surfaces, confirming their durability and applicability in the filtration of magnesium melts. The pre- and post-immersion cross sections of the AZ91 samples are evaluated by means of an automatic SEM to assess the presence of inclusions in the metal. The number of inclusions containing oxygen or nitrogen is notably lower for AZ91 samples that were in contact with Al₂O₃-C-, Al₂O₃-, or MgAlON-coated filters, showing the potential of these materials for the filtration of magnesium alloy melts.

1. Introduction

Due to its low density, high specific strength, and resource availability, magnesium and its alloys, such as AZ91, have a high potential for various lightweight applications. A major hindrance for its widespread processing and use is its high reactivity, contributing to high dross- and sludge formation in the melt, which results in the metal being prone to corrosion and containing high quantities of nonmetallic inclusions, if the handling of the melt has not been accurate. The inclusions can be divided into oxide films, lumps, and clusters, as well as intermetallic particles; gas- and shrinkage pores, may also be present. While measures are taken to protect and cleanse magnesium melts on industrial scale, such as gas purging treatments by Ar, N₂, or Cl₂, the usage of a variety of possible cover gases or fluxes and the optimization of the casting system toward a high grade of enclosure, the application of ceramic foam filters is seen as a promising method for cleansing the melt and improving the mechanical properties of the casting.

Ideally, an auxiliary addition of fluxes would be avoided, while delivering the same quality of melt cleanliness.

Wu et al. emphasized the effectiveness of ceramic foam filters made from MgO or Al₂O₃ in AZ91, improving the elongation-to-failure of cast samples up to relative 58%.

In contrast to oxidic, sintered filters, carbon-bonded ceramic foam filters show higher resistance toward thermal shock and creep deformation, as well as lower energy consumption during their manufacture, due to their lower manufacturing temperature.

After carbon-bonded alumina filters showed promising results in the filtration of steel melts, short-term immersion tests in AZ91 have been carried out to evaluate their applicability in a magnesium alloy melt. Interface reactions between the AZ91 melt and variously coated ceramic Al₂O₃-C filters have been investigated after immersion times of 10–120 s. The investigated filter coatings consisted of Al₂O₃, MgO-C, MgAl₂O₄, or carbon nanotubes/alumina nanosheets. The formation of MgO in situ layers was shown on filter surfaces containing Al₂O₃ or MgAl₂O₄. Therefore, the next step toward assessing the applicability of oxidic as well as carbon-bonded ceramic foam filters in the field of magnesium melt filtration is the evaluation of their long-term resistance toward the magnesium melt, with a special regard toward melt contamination and inclusion content.

In this study, additional ceramic foam filter materials, namely ZrO₂ and MgAlON, were added to the selected materials.

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tested previously,[16] and immersed into a primary AZ91 metal melt for up to 60 min.

MgAlON was shown to have sufficient resistance toward oxidation, even in its powdered state, it would only gradually start oxidation at temperatures beyond 750 °C.[18] Furthermore, Al–Mg alloys were shown to be nonwetting on its surface.[17]

Conventional SEM as well as automatic particle identification and analysis via an automatic SEM–energy dispersive X-ray analysis (EDX) device were applied to evaluate possible melt contamination or other changes in the particle contents of the AZ91 samples caused by the filter materials after the immersion tests.

2. Experimental Section

2.1. Preparation of the Filter Samples

The types of filter samples used for immersion testing in the magnesium alloy melt are shown in Table 1.

ZrO₂ ceramic foam filters were manufactured by Drache Umwelt GmbH (Diez, Germany).

The remaining filter sample types were based on Al₂O₃-C substrates.[14–19] The raw materials used for their manufacture were Al₂O₃ (66 wt%, Martoxid MR70, Martinswerk, Germany), the coal tar pitch binder Carbores P (20 wt%, Rütgers, Germany), graphite (7.7 wt%, AF96/97, Graphit Kropfmühl, Germany), and carbon black (6.3 wt%, Luvomaxx N991, Lehmann&Voss, Germany). Aqueous slurry was prepared, using the following additives: the temporary binder ammonium lignosulfonate (Otto-Dille, Germany), the dispersion agent Castament K1012 (Zschimmer&Schwarz, Germany). The slurry layers were applied onto a polyurethane foam template (10 ppi) via rolling and spray coating, as described by Schramm et al.,[20] following the Schwartzwalder technique.[21] After a drying period of 24 h at room temperature, the filter substrates were placed inside of petcoke-filled steel retorts and heat treated at 800 °C for 3 h, resulting in the pyrolysis of the PU foam template, leaving the carbon-bonded ceramic foam structure behind. The carbon-free Al₂O₃- or MgAlON coatings of the respective filter batches were applied onto the Al₂O₃-C substrates by means of spray coating, the aqueous Al₂O₃- or MgAlON slurries were prepared using the same additives as the substrates. After subsequent drying at room temperature, the coated filters were heat treated in a petcoke-filled alumina retort at 1400 °C for 5 h, following the heating regime described by Emmel and Aneziris.[19]

### Table 1. Filter materials evaluated via immersion testing in an AZ91 melt.

| Filter sample type, abbreviation | Material used for filter sample substrate | Material used for filter sample coating |
|---------------------------------|------------------------------------------|----------------------------------------|
| Al₂O₃-C                         | Al₂O₃-C                                  | –                                      |
| Al₂O₃-C + Al₂O₃                 | Al₂O₃-C                                  | Al₂O₃                                  |
| Al₂O₃-C + MgAlON[17]            | Al₂O₃-C                                  | MgAlON                                 |
| ZrO₂                            | ZrO₂                                     | ZrO₂                                   |

2.2. Immersion Tests

The experiments were conducted in the vertical tube furnace RHTV 120/600/18, made by Nabertherm (Germany). The temperature in the heating zone of the furnace was set to 680 °C and monitored constantly by means of a thermocouple, which was set in a corundum tube and placed on the same height as the stainless steel ladle (grade EN 1.4841), which contained the AZ91 magnesium alloy (9 wt% aluminium, 1 wt% zinc, and 0.2 wt% manganese).[1]

Before melting the AZ91 magnesium alloy, the furnace was evacuated and filled with a protective gas mixture consisting of Ar and 0.2 vol% SF₆. The gas flow was adjusted to 300 mL min⁻¹. After the alloy was molten, a steel strainer tool was used to remove as much of the slag layer from the melt surface as possible. This was done to reduce the amount of nonmetallic particles that would otherwise enter the melt during the immersion process of the ceramic filter samples, which are lowered into the melt through the surface previously covered in slag. Approximately 250 g of AZ91 were used for each immersion test series with each type of respective filter material.

While each filter sample was placed in the upper part of the furnace tube from above, suspended from a steel rod, the protective gas flow was increased to 850 mL min⁻¹, to expel any oxygen from the filter foam. After holding the filter sample in this position for 10 min, it was lowered into the heating zone of the furnace, ≈5 cm above the melt, to heat up for 10 min.

Four filter samples of each material type were used, getting immersed into the melt for 5, 15, 30, and 60 min, respectively. After each immersion test with one type of filter foam, the melt was left to settle for 30 min at 680 °C under protective gas, before the next filter sample was immersed.

Before and after the immersion of each filter foam, a magnesium alloy sample was taken from the melt with the help of a small stainless steel dipping ladle. The ladle was lowered into the melt and carefully moved to be filled with the metal, then left to cool down in the upper middle part of the furnace tube filled with protective Ar + 0.2 vol% SF₆ gas mixture to avoid oxidation.

Before the immersion testing of each filter material type, the respective melt used in the previous immersion tests with a different filter type was cooled down and removed, and the furnace cleaned and recharged with fresh AZ91 to be melted down. After the immersion tests, a layer of residue was found covering the inside of the furnace tube. A sample was taken of this residue and analyzed using an X-ray fluorescence analysis (XRF) device.

2.3. Evaluation of the AZ91 Samples

The magnesium alloy samples retrieved via dipping ladle after each immersion test were sectioned in the middle and prepared for SEM evaluation and EDX analysis (ESEM FEG XL30 by FEI Eindhoven, Netherlands, equipped with an EDX device by EDAX Ametek, USA). For this purpose, the surfaces of the metal samples (≈1 cm² each) were ground and polished with a silicon carbide medium.

After the respective immersion tests with a duration of 60 min, the solidified AZ91 samples were removed from the
stainless steel ladle. Samples measuring $60 \times 30 \times 15 \text{ mm}^3$ were cut from their middle section, ground, and polished using a diamond suspension to be evaluated by means of automated SEM–EDX analysis (ASPEX PSEM eXpress, FEI Eindhoven), scanning an area of $\approx 345 \text{ mm}^2$ per sample. The automatic feature analysis and evaluation were designed to yield statistical information on inclusions found on the polished surface of the sample, such as their size, morphology, and chemical elements present therein, quantifying and identifying metallic as well as nonmetallic inclusions. The device was equipped with a backscatter-electron detector (BSE), identifying respective particles due to their contrast differences compared with the metal matrix. Particles larger than 1 $\mu m$ were automatically identified by the setup; the concentration of registered particles per analyzed area was evaluated. The minimum distance between particles detected as individuals is 1 $\mu m$.[22] EDX spectroscopy was applied automatically to investigate the chemical composition of particles. It should be considered, that the activation volume of the electron beam was causing element counts from the underground matrix of the metal sample to appear.

To investigate the influence of the immersed filters on the cleanliness of the metal, an AZ91 sample for comparative ASPEX evaluation was cut from the AZ91 ingot (Magontech GmbH, Germany) that was used as raw material for these experiments. In the following, this comparative sample is referred to as “as-cast” AZ91 ingot sample, representing the state of the AZ91 before the immersion tests.

### 2.4. Evaluation of the Immersed Filter Samples

After its respective immersion time in the AZ91 melt, each filter sample was moved into the top section of the furnace to cool down under protective atmosphere, consisting of Ar + 0.2 vol% SF$_6$. Afterwards, the immersed filter samples were photographed (Figure 1) and evaluated by means of optical microscopy, using a Keyence digital microscope (VHX 2000D equipped with a VH-Z20R objective, having a magnification range of 20–200×), as well as scanning electron microscopy (SEM). For preparing the SEM samples, small sections were cut from the immersed part of the filter sample, which was in contact with the metal melt. The cut ceramic foam samples were sputtered with carbon to ensure conductivity and therefore avoid the nonconductive ceramic material getting charged by the electron beam, which would cause distortions in the micrograph.

### 3. Results and Discussion

#### 3.1. SEM Evaluation of the Immersed Filter Samples

For each type of immersed filter samples, finely structured layers were observed on the filter surfaces, that were in contact with the magnesium alloy melt. Magnesium, oxygen, as well as small quantities of fluorine and sulfur have been identified in these surface layers via EDX analysis, suggesting, that they mainly consist of magnesium oxide and small quantities of magnesium fluoride, the latter one resulting from the reaction of the magnesium alloy with the SF$_6$ present in the cover gas.[1] These layers show similarities to the ones observed in the previous study of Schramm et al.[16] This research had shown, that the MgO in situ layers were the result of Al$_2$O$_3$-containing filter surfaces reacting with the magnesium alloy melt, reducing the alumina content and forming finely structured MgO surface layers, which, in turn, have the potential to attract and bind oxide films, lumps, or clusters from the melt.[16] Furthermore, it can be concluded, that these layers were a direct result of the filter being in contact with the melt. It is safe to say, that these layers did not result from particles, which were present in the furnace atmosphere, settling on the filter surface during the cooling phase, as these layers were not observed on the upper sections of the filters, which were not in contact with the melt. The AZ91 droplets found on some of the immersed filter surfaces, which will be described in the following sections, showed a gleaming, metallic surface, uncontaminated by any comparable nonmetallic layers or particles, further strengthening this conclusion.

The XRF analysis of the layer sample found covering the furnace tube showed its composition to be $\approx 92$ wt% MgO, 7 wt% of sulfur-containing residue, originating from the reaction of the AZ91 surface with the SF$_6$ present in the cover gas, and 1 wt% of Zn-containing residue.

#### 3.1.1. Uncoated Al$_2$O$_3$-C filters after the Immersion Tests

Being evaluated by digital optical microscopy, the uncoated Al$_2$O$_3$-C filter immersed into the AZ91 melt for 5 min showed large portions of the surface being smooth and dimly reflective, covered in few patches of a white-grayish layer, the metallic residue on the border of the immersed area showing a yellowish hue, likely due to iron-containing impurities. After an immersion time of 15, 30, or 60 min, the area covered in the gray, raggedly structured layer was increased respectively, after an immersion time of 15 min, metallic particles have been observed on the filter surface by means of optical microscopy (Figure 2a). The layers

![Figure 1. Ceramic foam filter samples after their immersion in an AZ91 melt at 680 °C under protective Ar + 0.2 vol% SF$_6$ atmosphere for 60 min: (a) ZrO$_2$ filter foam, (b) uncoated Al$_2$O$_3$-C filter foam, (c) Al$_2$O$_3$-C filter foam coated in Al$_2$O$_3$, and (d) Al$_2$O$_3$-C filter foam coated in MgAlON.](image-url)
seen on the Al₂O₃-C filter surface were suggested to consist of MgO by means of EDX analysis, in accordance with the thermo-dynamic calculations carried out previously,[16] which showed the reaction of the alumina content of the filter surface with the magnesium alloy melt, resulting in the reduction of Al₂O₃ and the formation of MgO on the filter.

SEM observations showed finely structured MgO in situ layers with the grainy surface of the filter being visible underneath (Figure 2b). MgO platelets with lengths of $\approx 3 \mu m$ have been observed on the surface of the filter that has been immersed in the metal melt for 15 min (see Figure 2b).

After 30 and 60 min of being in contact with the AZ91 melt, similar, platelet-like MgO in situ layers to the ones observed in the previous study[16] could be seen, their thickness being around 3-5 μm, respectively (Figure 2c,d).

3.1.2. Al₂O₃-Coated Al₂O₃-C Filters after the Immersion Tests

SEM micrographs after an immersion time of 5 min show the formation of a finely structured MgO in situ layer[16] on the filter surface. This layer has a platelet- or coral-like morphology (Figure 3a) and appears in patches with thicknesses of $\approx 10–15 \mu m$. The coarser, grainy surface of the sintered Al₂O₃ coating is still clearly visible in areas uncovered by the in situ layer.

Similarly structured and denser layers of comparable thickness were found on the filter immersed in the AZ91 melt for 15 min as well, with the coarsely structured Al₂O₃ filter coating still being recognizable underneath (Figure 3b). Sulfur and fluorine were identified in the in situ layer by means of EDX analysis, their source being the reactions with the SF₆-containing cover gas.[11] The in situ layer found on the filter samples that were immersed in the melt for 30 min had a thickness ranging from 10 to 20 μm.

After an immersion time of 60 min, a few large metallic AZ91 droplets could be seen on the filter surface, ranging from 200 to 400 μm in diameter. A larger number of smaller AZ91 droplets could be found on the surface as well, having diameters of $\approx 3 \mu m$ (see Figure 3d). Areas covered in layers of MgO were found on the filter surface, other areas showed the Al₂O₃-coated surface, which was not covered by MgO. The observed AZ91 droplets (Figure 3d) were shown to be free of oxidic layers by means of EDX analysis.

3.1.3. MgAlON-Coated Filters after the Immersion Tests

After the immersion of the filter samples coated in MgAlON, relatively small areas covered in a finely structured in situ layer were found on the immersed part of the surface during SEM observation. EDX analysis showed, that these layers contain magnesium, aluminum, oxygen, fluorine and sulfur, suggesting their composition of MgO, MgF₂, and Al₂O₃; fluorine and sulfur contents originating from reactions with the SF₆-containing cover gas. Areas that were not covered in this layer showed the same, grainy structure that is seen in nonimmersed MgAlON, suggesting, that the coating was not eroded or damaged by the magnesium melt (Figure 4a). This shows the durability and applicability of the material for the usage in magnesium melt filtration. After an immersion time of 5 min, the MgAlON surface was notably
smooth with patches of MgO/MgF₂ accumulations on its surface, their composition suggested by EDX analysis.

Optical micrographs showed accumulations of metal residue, that solidified inside the macropores of the filter. Few metallic AZ91 droplets could be found on the surface of the filter sample immersed into the AZ91 melt for 15 min (Figure 4b). Their size was observed to be 50–70 μm. Small patches of MgO accumulations were found on the surface as well, having thicknesses of ≈15 μm and leaving the remaining MgAlON surface uncovered.

After an immersion time of 30 min, a larger quantity of MgO patches with a thickness of ≈20 μm was seen in the respective SEM micrograph, droplets of AZ91 with diameters up to 100 μm were found, some of them covered in few fine MgO platelets (Figure 4c,d) while mostly having a metallic shine, shown by the optical micrographs (cf. Figure 4f). After an immersion time of 60 min, a significantly larger number of various AZ91 droplets was found on the filter surface, their diameters ranging from 50 to 500 μm. These droplet accumulations were predominantly found in the region of firing cracks on the filter surface. Because of their surface structure, these regions were more advantageous for droplets to stay on, as nonferrous alloys were previously shown to be nonwetting on a MgAlON surface.²⁵²⁶²⁷²⁸²⁹³⁰ After an immersion time of 30 min, a larger quantity of MgO patches with a thickness of ≈20 μm was seen in the respective SEM micrograph, droplets of AZ91 with diameters up to 100 μm were found, some of them covered in few fine MgO platelets (Figure 4c,d) while mostly having a metallic shine, shown by the optical micrographs (cf. Figure 4f). After an immersion time of 60 min, a significantly larger number of various AZ91 droplets was found on the filter surface, their diameters ranging from 50 to 500 μm. These droplet accumulations were predominantly found in the region of firing cracks on the filter surface. Because of their surface structure, these regions were more advantageous for droplets to stay on, as nonferrous alloys were previously shown to be nonwetting on a MgAlON surface.²⁵²⁶²⁷²⁸²⁹³⁰

3.1.4. ZrO₂-Coated Filters After the Immersion Tests

By means of SEM observation, finely structured, patchy layers were found on the surfaces of ZrO₂-filters that were immersed in the AZ91 melt for 5–15 min, EDX analysis suggested their composition to be MgO and small quantities of MgF₂, their thickness ranging from 10 to 20 μm, respectively. Manufacturing cracks were present on the surface of the filter material, its coarsely grained surface being recognizable (Figure 5a,b).

The areas of MgO-layers were spread wider after an immersion time of 30 min, having thicknesses up to 20 μm, with the coarse ZrO₂ surface still being visible underneath (Figure 5c).

After 60 min of contact with the AZ91 melt, a similarly structured layer of MgO was found on a larger portion of the ZrO₂ filter surface, traces of fluorine were found by means of EDX analysis as well. The layer had a maximum thickness of ≈50 μm. Furthermore, EDX evaluation showed that magnesium was also present in the areas of the filter surface, which was not covered by the in situ layer, suggesting a reaction of ZrO₂ with the metallic magnesium, resulting in small quantities of magnesium being absorbed into the ceramic material, considering the fact that magnesium is commonly used as a stabilizing agent for ZrO₂.¹²

The Zr peak of the EDX analysis was smaller for thick in situ layers, whereas thinner in situ layers showed a higher Zr peak, attributed to the signals from the intact filter material underneath.
3.2. SEM Evaluation of the AZ91 Samples

The observations made on the polished cross-sections of the AZ91 samples taken from the AZ91 melt before and after the immersion of each filter were similar. Closer to the edge of the sample, shrinkage porosity was observed (Figure 6a), furthermore, manganese-rich particles were visible, as well as the structure of the intermetallic \( \beta \)-phase \((\text{Mg}_{17}\text{Al}_{12})\),\(^3\) which was observed along the grain boundaries. Similar Mn- and Fe-rich particles found in AZ91 were characterized by Øymo et al.,\(^{24}\) describing their composition as \(\text{Al}_8(\text{Mn, Fe})_5\).

No significant amount of oxidic particles was found on the cross section of the samples during manual SEM analysis, suggesting, that the ceramic filters did not pollute the melt. Figure 6 shows a selection of SEM micrographs, with the observed structures marked.

3.3. ASPEX Evaluation of the AZ91 Samples

3.3.1. Basic ASPEX Evaluation

The rule file, which was used for the classification of the particles found during ASPEX evaluation, is shown in Table 2. It shows the setup of restrictions that were chosen to distinguish detected particles based on their chemical composition. The main focus is put onto inclusions containing oxygen or nitrogen,\(^{24}\) as these nonmetallic inclusions are regarded as problematic. They are introduced into the magnesium alloy melt because of its high reactivity with any technologically unavoidable, oxidizing components left in the furnace atmosphere.\(^1\) Nonmetallic inclusions impair the mechanical properties of the castings notably.\(^{11}\) An overview of the various particle groups and their quantities found on the respective AZ91 sample cross-sections is shown in Table 3.
It should be noted that the characteristic intermetallic phase, which is distributed in a net-like way along grain boundaries (cf. Figure 6), was also registered during ASPEX analysis due to its contrast to the matrix of the AZ91 alloy. The amount of the intermetallic phase was similar for every immersion-tested AZ91 sample, regardless of the filter material immersed. The
average chemical composition of these registered intermetallic phases is shown in Table 4. The comparison of the average element contents of Al, Mg, and Mn present in both classes of registered intermetallic phases shows comparable amounts for the samples that were in contact with the respective filters (see Table 4). Therefore, it can be assumed, that the tested types of ceramic filters do not have a significant impact on the compositions of intermetallic phases that are typical for the alloy. Furthermore, around 90% of the evaluated intermetallic phase of the immersion-tested samples was shown to contain up to 2 wt% of iron for each respective AZ91 sample. It should be noted, that the “as-cast” AZ91 ingot sample contains a lower average amount of iron at around 0.7 wt% (see Table S1, Supporting Information) and a significantly higher amount of iron-free intermetallic phase (48.7%) compared to the immersion-tested samples, which contained average iron-free intermetallic amounts of only 7% (see Table 4). Therefore, it can be concluded, that the additional amount of iron entered the melt through its contact with the stainless steel ladle (see Section 2.2) during the immersion tests, increasing the amount of iron-containing intermetallic phases in the process. The high standard deviations seen for the magnesium and aluminum contents can be explained by considering the activation volume of the electron beam during the ASPEX process, causing counts from the underlying magnesium matrix, which can be locally fluctuating, depending on the size and composition of the evaluated particle.

No zirconium-containing inclusions were found on the AZ91 surfaces of the “as-cast” ingot sample and the samples that were in contact with Al2O3-C-, Al2O3-, or MgAlON surfaces, therefore it can be concluded, that no Zr impurities were present in the AZ91 melt prior to the immersion experiments. The ASPEX analysis of the AZ91 sample, which has been in contact with the ZrO2 filter, showed that contamination of the melt with Zr-containing particles can be seen as negligible—overall, only 4 of such particles with sizes ranging from 0.5 to 12.6 μm2 could be found on the evaluated sample cross section of 345 mm2. Aside from an average of 6 wt% zirconium, these particles contained averagely 6.1 wt% carbon, 3.1 wt% oxygen, 59.9 wt% magnesium, 17.9 wt% aluminum, and 4.7 wt% silicon (see Table S2, Supporting Information).

The amount of sulfur registered in the inclusion groups is shown to be very low, never exceeding an average of 0.2 wt% (see Table S2, Supporting Information). Therefore, it is possible to conclude, that particles containing sulfur from the reaction with the Ar/SF6 cover gas on the melt surface did not get transported into the melt to contaminate it significantly.

### Table 2. Rule file used for the characterization of particle groups.

| Particle class | Restrictions |
|----------------|--------------|
| Zr-containing inclusions | O > 0 and Zr > 0 |
| Inclusions containing oxygen (Zr-free) | O > 0 |
| Inclusions containing nitrogen | N > 0 |
| Mn-Al-Mg intermetallic phase (containing Fe) | Mn > 0 and Al > 0 and Fe > 0 |
| Mn-Al-Mg intermetallic phase (Fe-free) | Mn > 0 and Al > 0 and Fe = 0 |
| Other inclusions | Particles not belonging to previous classes |

### Table 3. Number of relevant inclusions found on the cross section of the AZ91 samples after 60 min of immersion time of the respective filter material.

| Particle class of interest | Number of inclusions found on the AZ91 sample cross section [Normalized to 100 mm2 of searched area] |
|----------------------------|-------------------------------------------------------------------------------------------------|
| “As-cast” AZ91 ingot filter immersed | Al2O3-C | Al2O3-C + ZrO2 | Al2O3-C + MgAlON filter immersed |
| Zr-containing inclusions | 8 | 18 | 0 |
| Oxides (Zr-free) | 6 | 15 | 25 |
| Nitrides | 9 | 12 | 13 |
| Other inclusions | 10 | 12 | 11 |
| Mn-Al-Mg intermetallic phase (containing Fe) | 30 | 33 | 29 |
| Mn-Al-Mg intermetallic phase (Fe-free) | 30 | 33 | 29 |

### Table 4. Composition of iron-free and iron-containing intermetallic phases found on the cross section of the AZ91 samples after the immersion tests, determined via automatic SEM and EDX analysis. The percentage of intermetallic particles is given in relation to the total amount of particles registered on the respective sample cross section.

| Filter sample immersed | Al [wt%] | Mg [wt%] | Mn [wt%] | Fe [wt%] | % of all particles registered |
|------------------------|---------|---------|---------|---------|-------------------------------|
| “As-cast” AZ91 ingot sample | 21.7 ± 2.1 | 7.3 ± 6.4 | 67.2 ± 6.3 | 1.7 ± 0.5 | 39.5 |
| | 24.6 ± 3.9 | 11.7 ± 11.3 | 63.3 ± 12.5 | 0 | 48.7 |
| Al2O3-C | 28.8 ± 5.5 | 10.1 ± 8.5 | 59.1 ± 8.5 | 1.9 ± 0.5 | 81.6 |
| | 34.4 ± 8.1 | 24.2 ± 16.6 | 40.3 ± 18.3 | 0 | 7.8 |
| Al2O3-C + Al2O3 | 28.8 ± 6.9 | 11.7 ± 8.6 | 57.8 ± 9.1 | 1.6 ± 0.4 | 69.1 |
| | 32.5 ± 8.6 | 19.3 ± 15.0 | 47.6 ± 15.8 | 0 | 6.5 |
| Al2O3-C + MgAlON | 27.9 ± 4.9 | 9.6 ± 7.7 | 60.4 ± 7.5 | 1.9 ± 0.5 | 76.9 |
| | 32.3 ± 7.7 | 18.2 ± 13.4 | 48.9 ± 16.5 | 0 | 8 |
| ZrO2 | 29.0 ± 7.5 | 14.3 ± 9.9 | 54.5 ± 9.1 | 2.0 ± 0.6 | 67.7 |
| | 32.0 ± 9.2 | 29.3 ± 16.3 | 37.6 ± 15.8 | 0 | 5.7 |
3.3.2. Oxygen-Containing Particles

An average number of 306 oxygen-containing particles was registered on the cross section of the AZ91 "as-cast" ingot sample per 100 mm², having particle sizes up to 50 μm². After the immersion tests, significantly lower numbers of oxygen-containing inclusions were found for the AZ91 samples that were in contact with the Al₂O₃-C- or Al₂O₃-coated filters, while their number stayed nearly constant for the "MgAlON-immersed"-sample. The "ZrO₂-immersed" AZ91 sample was the only one to display a higher number of such inclusions after the immersion test (see Table 3), inclusions smaller than 10 μm² remaining nearly constant after the ZrO₂-filter contact, whereas the amount of larger inclusions increased notably (see Table S3, Supporting Information and Figure 7).

The respective diagram (Figure 7) shows, that the number of oxygen-containing particles of certain sizes is largely reduced after the immersion of the other filter types, the "as-cast"

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**Figure 7.** Size distribution of particles found on the cross section of AZ91 samples before and after the immersion of the respective filter materials (cf. Table S3, Supporting Information).
AZ91 sample being the comparative benchmark: after the \( \text{Al}_2\text{O}_3 \)-C-immersion, the amount of particles smaller than 50 \( \mu \text{m}^2 \) is significantly reduced, immersion of the \( \text{Al}_2\text{O}_3 \)-coated filter resulted in a notable decrease in particles smaller than 30 \( \mu \text{m}^2 \), while a few particles with sizes around 50 \( \mu \text{m}^2 \) seemed to have been introduced into the metal. For the AZ91 sample that has been in contact with the MgAlON-filter, the amount of inclusions smaller than 10 \( \mu \text{m}^2 \) decreased notably, whereas there has been a slight increase in particles up to 80 \( \mu \text{m}^2 \), two particles reaching 130 \( \mu \text{m}^2 \) in size. The introduction of a number of these larger particles can be explained with the manual removal of the slag layer covering the surface of the melt by means of a stainless steel strainer prior to the immersion process, described in Section 2.2. Technologically, it was not possible to fully exclude a small number of remaining particles getting introduced into the melt while the respective filter sample was entering it through the surface previously covered by slag.

For the AZ91 samples that were in contact with the \( \text{Al}_2\text{O}_3 \)-C, \( \text{Al}_2\text{O}_3 \)-, or MgAlON-coated filters, the majority of oxygen-containing particle sizes was below 20 \( \mu \text{m}^2 \).

The average sizes of the oxygen-containing particle group ranged from 8.5 to 27.8 \( \mu \text{m}^2 \), the smallest average size being registered on the surface of the AZ91 sample that was in contact with the \( \text{Al}_2\text{O}_3 \)-filter coating, the largest—for the sample that has been in contact with the \( \text{ZrO}_2 \) filter (see Table S3, Supporting Information).

In regards to the inclusion group containing oxygen, the results of the ASPEX analysis showed that the average amount of oxygen present in these particles did not exceed average values of 1.6–2.6 wt% for all AZ91 samples that had filters immersed in them, whereas the amount of oxygen in this particle group was as high as 10.3 wt% for the “as-cast” AZ91 ingot sample (Table S2, Supporting Information).

The highest average amount of oxygen in immersion-tested samples was found in the sample that had the \( \text{ZrO}_2 \) filter immersed, whereas the lowest amount was noted for the sample that was in contact with the \( \text{Al}_2\text{O}_3 \)-coated carbon-bonded alumina filter. It should furthermore be noted, that the AZ91 sample that has been in contact with the \( \text{ZrO}_2 \) filter had the overall largest average inclusion size at 39 \( \mu \text{m}^2 \) (see Table S1, Supporting Information). This corresponds with the conclusion of Wu et al.,\cite{13} stating that the \( \text{ZrO}_2 \) filters showed a lower efficiency in practical filtration experiments than \( \text{Al}_2\text{O}_3 \) filters.

SEM observations of MgO in situ layers made on the respective \( \text{Al}_2\text{O}_3 \)-C-, \( \text{Al}_2\text{O}_3 \)-, and MgAlON-filter surfaces after their immersion (see Section 3.1) suggest, that a significant number of oxygen-containing inclusions present in the AZ91 melt was attracted and subsequently bound to their filter surfaces, effectively getting removed from the metal melt.

The carbon content registered in the oxygen-containing inclusion group was highest for the AZ91 sample that was in contact with the uncoated \( \text{Al}_2\text{O}_3 \)-C-filter, reaching an average of 2.9 wt%, while the other samples, which were in contact with coated filters, showed lower values. The lowest carbon content of 0.5 wt% was registered for the “MgAlON-immersed” sample.

The relatively low total oxygen contents of around 0.1 wt% (see Table S1, Supporting Information) and numbers of registered particles on the cross section of the immersion-tested AZ91 samples (see Table 3), compared with the “as-cast” AZ91 ingot benchmark with a total average oxygen content of 0.4 wt%, show that the filter samples do not contaminate the AZ91 melt with nonmetallic inclusions. On the contrary, a tendency is seen, that the selected filters tend to lower the number of inclusions as well as the overall oxygen content of said particles, the only exception being the \( \text{ZrO}_2 \) filter immersion, which resulted in a higher number of oxygen-containing inclusions.

### 3.3.3. Nitrogen-Containing Particles

Apart from the registered intermetallic phases, the inclusion group classified as being nitrogen-containing showed the largest number of particles found on the cross-section of the “as-cast” AZ91 ingot sample—an average of 666 particles was registered per 100 mm\(^2\) of its evaluated cross section. After the immersion tests, the number of nitrogen-containing inclusions was significantly decreased for all immersion-tested samples. The number of nitrogen-containing particles after immersion testing was significantly lower compared with the oxygen-containing ones—with particle numbers ranging from a minimum of 81 to a maximum of 120 particles per 100 mm\(^2\) being noted for the AZ91 samples that were in contact with the \( \text{ZrO}_2 \)- and \( \text{Al}_2\text{O}_3 \)-coated filters, respectively (Table 3). These particles had sizes ranging from 0.1 to 500 \( \mu \text{m}^2 \), their majority being smaller than 50 \( \mu \text{m}^2 \) (Figure 7). A small number of inclusions larger than 50 \( \mu \text{m}^2 \) was detected after the immersion tests that was not observed on the cross section of the “as cast” AZ91 ingot sample. These inclusions are suggested to originate from technologically unavoidable slag residue introduced into the melt by the immersion process, as described in Section 3.3.2 for the oxygen-containing particles.

The average size of this inclusion group was observed to be between 33.4 and 51.3 \( \mu \text{m}^2 \), the values having been registered for the samples that have been in contact with MgAlON or \( \text{ZrO}_2 \), respectively (cf. Table S3, Supporting Information). The average nitrogen content of the inclusion group was 1.5 wt% for all samples, an exception being the \( \text{ZrO}_2 \)-immersion-tested AZ91 sample, containing an average of only 0.1 wt% nitrogen.

It can be noted, that the amounts of magnesium, aluminum, and manganese in the nitrogen-containing inclusion group are similar for all AZ91 samples, regardless of the filter materials immersed in them.

The average total nitrogen content of 0.1 wt% was similar for the immersion-tested samples as well as the “as-cast” AZ91 ingot sample (cf. Table S3, Supporting Information), reaching a maximum of 1.6 wt% for inclusions specifically classified for their nitrogen content (cf. Table 2).

### 3.3.4. Inclusions Classified as “Other”

The inclusion group classified as “Other” in the rule file (see Table 2 and Figure 7) was shown to consist of a small number of intermetallic particles that did not exceed sizes of 10 \( \mu \text{m}^2 \), the majority being smaller than 3 \( \mu \text{m}^2 \) (see Figure 7). The largest number of inclusions in this group was found on the cross section of the AZ91 sample, which was in contact with the uncoated \( \text{Al}_2\text{O}_3 \)-C filter, with only 17 particles per 100 mm\(^2\) registered. None of the particles of this group contained nitrogen, oxygen,
or manganese. Regardless of the filter material immersed in the respective AZ91 sample, the inclusion group contained similar amounts of magnesium (around 65 wt%) and aluminum (around 28 wt%), only negligible traces of iron and sulfur were found. The carbon content of the inclusion group was below 1.5 wt% for all samples. For the “as-cast” AZ91 ingot sample, only four of the intermetallic inclusions classified as “Other” were found, containing 91 wt% of Mg and 6 wt% of Al.

4. Conclusion

In this study, immersion tests of variously coated carbon-bonded alumina-, as well as ZrO₂- filters were conducted in an AZ91 melt for up to 60 min at 680 °C under protective Ar + 0.2 vol% SF₆ atmosphere. The filters as well as AZ91 samples were evaluated by means of optical microscopy and SEM. Automated SEM analysis was applied for the evaluation of inclusions on the cross sections of the AZ91 samples after the immersion tests with a duration of 60 min. The following conclusions can be drawn.

All of the ceramic foam filters were retrieved from the AZ91 melt undamaged and layers consisting mainly of MgO could be found on the filter surfaces after the immersion tests. Increased immersion times resulted in a tendency toward the buildup of thicker oxide layers on the filter surfaces, reaching up to 50 μm after an immersion time of 60 min.

AZ91 samples, which were in contact with Al₂O₃-, Al₂O₃-coated, and MgAlON-coated ceramic foam filters, were shown to have a lower amount of oxygen- and nitrogen-containing inclusions compared with the “as-cast” AZ91 ingot sample. The reduction of the number of inclusions, which were smaller than 20–30 μm² was most notable. This shows the potential of these ceramic filter materials for the successful application in magnesium alloy melt filtration. The filter materials do not seem to have an influence on the composition of the intermetallic phases of the alloy.

The cross section of the AZ91 sample, which was in contact with the ZrO₂ filter, showed the largest average inclusion sizes and a higher number of oxygen-containing inclusions, compared with their amount in the “as-cast” AZ91.

This leads to the conclusion of the ZrO₂ filter being the least effective material, which does not show promising potential for the filtration of magnesium alloy melts.

Future research into the formed in situ layers on the immersed filter surfaces is planned to identify any nonmetallic inclusions that were absorbed into the in situ layer from the AZ91 melt. Focused ion beam (FIB)-SEM analysis will be applied for this purpose.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study is available in the supplementary material of this article.

Keywords

carbon-bonded alumina, ceramic foam filters, immersion, inclusions, magnesium, MgAlON

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