Formation of Interface Layers between Corundum-Based Refractory Ceramics with Carbon Additions and Molten 42CrMo4 Steel

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The formation of reaction layers between corundum-based (Al2O3 + C) filter materials covered with functional Al2O3−C coatings having different carbon contents and molten steel 42CrMo4 is investigated at the reaction temperature of 1600 °C. Within the first 60 s, an amorphous reaction layer is formed at the interface between the original filter surface and the molten steel. This layer consists mainly of Fe and O with small, varying amounts of Al and Si. After a longer contact time (120 s), nanocrystalline phases, which are identified as iron-based oxides, formed within this amorphous interlayer. After 5 min, the amorphous interface layer is replaced by a dense corundum layer, on which thin corundum platelets are attached. The formation of the amorphous interface layer, its transformation to dense corundum, and the effect of the carbon content in the functional Al2O3−C coating on the nucleation and growth of the corundum platelets are discussed. The reaction experiments are carried out in a spark plasma sintering device to avoid liquid metal convection and as immersion tests in a steel casting simulator to obtain relevant information about the filtering process.

1. Introduction

Carbon-bonded alumina (Al2O3−C) is a material that is often used for production of ceramic foam filters for the filtration of steel melts.[3] The original idea behind the carbon addition was to improve the high-temperature mechanical properties of alumina filters,[2,4–6] their thermal shock resistance (through a higher thermal conductivity),[4,5] and their resistance against crack initiation.[6] Later on, it turned out that the addition of carbon to alumina also enhances the filtration efficiency for nonmetallic inclusions, which are often filtered by functional coatings on the basis of mullite, MgAl2O4 spinel, or carbon-bonded MgO.[7,8] For the filtration of alumina inclusions in deoxidized (Al-killed) 42CrMo4 steel, the best performance of functional Al2O3−C coatings was reported for the carbon content of about 4 mass% C.[9] Though the chemical and phase composition of the functional coatings are generally accepted as crucial factors influencing the agglomeration of the alumina inclusions and their adherence to the functionalized filter surface,[7,8,10–12] the mechanisms behind this filtration process were not fully explained yet.

In analogy to the clogging of the Al2O3−C entry nozzles used for the steel casting,[13–17] it is assumed that the carbon-bonded alumina reacts with molten steel by forming a new interface layer, which can attract and embed nonmetallic inclusions. A previous study of the interfacial reactions between the 42CrMo4 steel melt and the Al2O3−C metal melt filters, which were coated with open porous, carbon-free corundum, revealed that the interface layer forms in two consecutive steps.[9] In the first step, a thin continuous layer develops, which serves in the second step as a substrate for the nucleation and growth of polycrystalline corundum. It was observed that the continuous layer grows only, as long as the open pores in the original functional coating are preserved. When the open pores are closed by the new compact coating, the growth of the continuous layer finishes and the growth of corundum platelets starts.

At a normal pressure, alumina is known to be reduced by carbon to metallic aluminum at the temperatures above 2100 °C.[18–20] The by-product of this carbothermic reaction that is used as a nonelectrochemical alternative to the Hall–Héroult process is carbon monoxide. This reaction is usually described as \( \text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Al} + 3\text{CO} \). When a mixture of carbon and corundum is exposed to molten steel (in Ar atmosphere under normal pressure), the onset temperature of the carbothermic reduction of corundum is lowered to 1550 °C.[21,22]

After a critical evaluation of the results of Khanna et al.,[21] Zienert et al.[23] suggested, based on the thermodynamic calculations, an alternative reaction mechanism to the reaction \( \text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Al} + 3\text{CO} \) from previous studies.[18–22] According to Zienert’s thermodynamic model,[23] corundum is partially dissolved by liquid iron rather than reduced by carbon, when a mixture of Al2O3 and C is brought in contact with iron melt. During this reaction, no stable equilibrium between alumina and liquid iron is reached, because the CO gas, which develops permanently as a product of the reaction between

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dissolved oxygen and carbon, partially leaves the reaction zone. Consequently, alumina is constantly dissolved in liquid iron, which increases the concentration of aluminum in the melt. It is worth noting that another source of oxygen for the CO gas production is the oxygen solved in the steel melt. Therefore, the CO formation contributes to a “reactive” deoxidation of the molten steel, whereas the CO bubbles entrap and remove nonmetallic inclusions actively.\(^{[25,26]}\)

The increase in the amount of dissolved Al in the reaction zone is regarded as the main reason for the formation of secondary corundum on the surface of the Al\(_2\)O\(_3\) – C filter ceramics. However, the existing models cannot explain the nature of the second phase. After a pyrolysis step at 800 °C, the filter substrates contained 30 mass% C, the double-coated (recoated) filters 4 mass% C or no carbon, respectively. All filter materials under study (single-coated and double-coated) were microporous with the pore sizes ranging from 0.03 to 0.32 μm (single-coated) and from 0.47 to 0.82 μm (within the second coating). The open porosity ranged between 35 and 39 vol% as revealed by the mercury porosimetry (cf. the study by Emmel and Aneziris\(^{[27]}\)).

Afterward, some of these Al\(_2\)O\(_3\) – C substrate filters were spray coated again to produce functional coatings with different carbon contents. The coating thickness was 20–50 μm. The slurry used for this second spray-coating process contained a mixture of two different types of alumina (75 mass% Martoxid MR 70 by Martinswerk, Germany; 25 mass% of CL 370 by Almatis, Germany) with the addition of either a smaller amount of Carbores P than in the first coating process or without any carbon source. Table 1 shows the chemical compositions of the alumina powders, which were used for the filter production.

In the last step, the (single-coated) virgin Al\(_2\)O\(_3\) – C filter substrates and the filters recoated with slurries with different C/Al\(_2\)O\(_3\) ratios were annealed at 1400 °C. Finally, the substrate filters contained 30 mass% C, the double-coated (recoated) filters 4 mass% C or no carbon, respectively. All filter materials under study (single-coated and double-coated) were microporous with the pore sizes ranging from 0.03 to 0.32 μm (single-coated) and from 0.47 to 0.82 μm (within the second coating). The open porosity ranged between 35 and 39 vol% as revealed by the mercury porosimetry (cf. the study by Emmel and Aneziris\(^{[27]}\)). Molds used for the SPS process were produced in the same way. After applying the same heat treatments, the chemical composition and porosity of the moulds were equal to the chemical composition and porosity of the filter ceramics.

### 2. Experimental Section

#### 2.1. Filter Ceramic Production and Functionalization

The main body of the Al\(_2\)O\(_3\) – C filter ceramics was produced from prismatic polyurethane filter templates (125 × 20 × 20 mm\(^3\)) that were initially impregnated and additionally spray coated. The impregnation and spray slurries had the same composition but different contents of solid additives, mainly α-alumina (Martoxid MR 70, Martinswerk, Germany)\(^{[7,9]}\). As the main carbon source in the slurry, the modified coal tar pitch Carbores P was used to reduce the toxicity of the carbon containing binder. The full composition of the slurries was described in the study by Schmidt et al.\(^{[9]}\). After a pyrolysis step at 800 °C, following the Schwartzwalder processing route and the procedures from previous studies\(^{[5,9,24]}\) strut thicknesses of about 0.5 mm were achieved. The Al\(_2\)O\(_3\) – C substrates contained 30 mass% of carbon.

#### 2.2. Reaction Experiments

As reaction counterpart to Al\(_2\)O\(_3\) – C, steel 42CrMo4 (in form of powder with particle size < 45 μm, TLS Technik GmbH & Co., Spezialpulver KG, Germany) was used. The chemical composition of the steel is shown in Table 2. Prior to the SPS experiment, the ceramic molds having an outer diameter of 20 mm and a cavity diameter of ≈15 mm were filled with cut pieces (<15 mm) of the prismatic ceramic filters and steel powder, and served as vessels for the molten steel.\(^{[27]}\) The SPS reaction experiments were carried out in a HPD 25 (FCT Systeme GmbH, Germany). The SPS apparatus was evacuated to the residual pressure below 5 Pa and heated to 1600 °C with the heating rate of about 950 K min\(^{-1}\). During the SPS experiment that was conducted with continuously operated vacuum pumps, the pressure was monitored to detect the gas release from the samples. For heating, conventional SPS graphite tools were used. The dwell

### Table 1. Chemical compositions of the two types of the alumina powders used in the ceramics production as provided by the supplier.

| Table 1. Chemical composition of the used steel alloy 42CrMo4 as provided by the powder vender. |
|-----------------------------------------------|
| Element | C | Cr | Mo | Si | Mn | Fe |
| Mass%   | 0.4 | 1.0 | 0.2 | 0.2 | 0.7 | Balance |
| Particle size | <5 μm |  |  |  |  |  |

**Table 1.** Chemical compositions of the two types of the alumina powders used in the ceramics production as provided by the supplier.

| Alumina type (supplier) | Composition [mass%] | Particle size |
|-------------------------|---------------------|---------------|
|                         | Na\(_2\)O | Fe\(_2\)O\(_3\) | SiO\(_2\) | CaO | MgO | Al\(_2\)O\(_3\) |  |
| Martoxid MR 70 (Martinswerk, Germany) | ≤0.1 | 0.02 | 0.08 | 0.02 | 0.06 | Balance | <5 μm |
| CL 370 (Almatis, Germany) | <0.14 | <0.04 | <0.07 | <0.03 | – | Balance | <10 μm |
times were 1, 5, and 30 min. As the SPS electrodes were cooled by water, cooling rates of several hundred K min\(^{-1}\) were reached.

Auxiliary experiments were conducted in a steel casting simulator, where the prismatic samples (125 × 20 × 20 mm\(^3\)) were immersed for 2 min in the same steel at a temperature of about 1600 °C. During the tests in the steel-casting simulator, the steel melt streamed on the rotating filter, which generated even higher heating rates close to thermal shock. High cooling rates were achieved by cooling down the samples in a chamber floated by argon.\(^9\)

2.3. Microstructure Characterization Methods

On the microscopic scale, the products of the chemical reaction between the molten steel and the surface of the ceramic filter were analyzed using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) and electron backscatter diffraction (SEM/EBSD). The elemental analysis using SEM/EDX was complemented by the electron probe microanalysis with wavelength dispersive X-ray spectroscopy (EPMA/WDX). For SEM/EDX/EBSD, a high-resolution SEM LEO-1530 (Carl Zeiss AG, Germany) with field-emission cathode, an EDX detector (Bruker AXS), and a Nordlys II EBSD detector (HKL Technology) was used. The SEM/EDX/EBSD experiments were carried out at an acceleration voltage of 20 kV. The working distance for EBSD was 15 mm, the tilting angle 70°, and the step size 0.3 μm. The software package Channel 5 (HKL Technology) was used for identification of the Kikuchi patterns and for the evaluation of the measured data. For the EPMA/WDX measurements, an electron probe microanalyzer JXA-8230 SuperProbe (Jeol GmbH, Germany) with five-crystal spectrometers was used.

On the nanoscale, the samples were characterized using transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy dispersive X-ray spectroscopy (EDX/TEM). These analyses were done in a JEM 2200 FS transmission electron microscope (JEOL Ltd., Japan) at an acceleration voltage of 200 kV. The TEM samples were prepared by the focused ion beam method (FIB) with a Helios NanoLab 600i (FEI, USA) in form of thin slices.

3. Results

3.1. Formation of a Thin Layer on the Surface of the Functionalized Al\(_2\)O\(_3\)─C Coatings

The early stages of the interface reactions were investigated in ceramic samples that were in contact with the steel melt for 1 min at 1600 °C. The TEM micrograph taken at the interface between the corundum coating without carbon and the solidified 42CrMo4 steel revealed the presence of an intermediate layer having the thickness between 100 and 200 nm (Figure 1a). According to SAED, this layer was amorphous (Figure 1b). The EDX analyses, which were done in the scanning TEM mode, showed that the interlayer consists mainly of O (about 50 at%) and Fe with small amounts of Si and Al as additional elements. The concentrations of the metallic elements, especially Si and Al, fluctuate strongly over the analyzed area. In the amorphous Fe–Al–Si–O layer, a single-crystalline MgAl\(_2\)O\(_4\) particle was embedded (Figure 1a,c), which stems from the reaction between

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**Figure 1.** a) TEM micrograph of an interface layer formed between solidified steel 42CrMo4 and a carbon-free functional corundum coating. The reaction experiment was carried out in SPS apparatus. The dwell time at 1600 °C was 1 min. b) SAED pattern of the interface layer. c) SAED of an MgAl\(_2\)O\(_4\) particle embedded in the amorphous layer.
MgO (contamination of alumina used for production of the filter ceramics, cf. Table 1) and corundum.\[29\] The solidified steel possesses the body-centered cubic (BCC) α-Fe structure (space group \textit{Im\textbar 3m}) with the lattice parameter \(a = 2.87\ \text{Å}\) as expected. Corundum (\(\alpha\text{-Al}_2\text{O}_3\)) with the space group \(\bar{R}\text{3c}\) and with the lattice parameters \(a = b = 4.75\ \text{Å}\) and \(c = 12.98\ \text{Å}\) was identified unambiguously on the other side of the amorphous coating.

A similar reaction layer was also found for \(\text{Al}_2\text{O}_3\text{─C}\) coating with 4 mass\% C (Figure 2a), which was in contact with the molten steel in the SPS for 1 min at 1600 °C. Also in this case, the interlayer was amorphous (cf. SAED in Figure 2b) and consisted, according to the results of the EDX analysis, of O, Fe, Al, and Si. However, in contrast to the \(\text{Al}_2\text{O}_3\) coating without carbon, where only random concentration fluctuations were observed, the interlayer grown between the \(\text{Al}_2\text{O}_3\text{─C}\) coating with 4 mass\% C and the steel possesses a mesoscopic composition gradient, which superimposes the local concentration fluctuations. Near the original filter surface, the amorphous interlayer contained about 32 at\% O, 30 at\% Al, 24 at\% Si, and 13 at\% Fe.

Close to the interface with the steel, the amorphous interlayer contained 46 at\% of O, 30 at\% of Si, 23 at\% of Fe, and only traces of Al. The local concentration fluctuations are evidenced by the absorption contrasts in the TEM micrograph (Figure 2a) and by presence of a small particle of α-Fe within the reaction layer (Figure 2c).

This distribution of the elements can be explained by a model that involves the reaction mechanism proposed by Zienert et al.\[23\] The amorphous layer is formed, after \(\text{Al}_2\text{O}_3\) is reduced by iron coming from the molten steel. The oxide layer is probably present in a solid state at the process temperature (1600 °C), because it contains a high amount of Al near the \(\text{Al}_2\text{O}_3\text{─C}\) coating. In analogy to the high melting temperature of hercynite (\(\text{FeAl}_2\text{O}_4\), 1740 °C),\[30,31\] it can be assumed that a higher Al concentration increases the melting temperature of the amorphous layer in comparison with a layer consisting of Al-free iron oxides. Also, a high concentration of Si can increase the melting temperature of the reaction layer, due to the high melting point of amorphous SiO\(_2\) (1713 °C).\[32\] Aluminum diffuses through the amorphous interlayer toward the melt. Consequently, its concentration is the highest near the \(\text{Al}_2\text{O}_3\text{─C}\) coating and the lowest at the interface to the former steel melt.

The observed differences in the oxygen concentration can be explained by the reaction of O with C to gaseous CO. In the vicinity of the \(\text{Al}_2\text{O}_3\text{─C}\) coating, the oxygen produced during the decomposition of \(\text{Al}_2\text{O}_3\) reacts with the carbon more intensely than on the opposite side of the amorphous layer, which leads to the opposite concentration gradient in comparison with the gradient of the Al concentration. This effect was understandably not observed in the \(\text{Al}_2\text{O}_3\) coating without C, where the reaction between C and O occurs preferentially in the main body of the \(\text{Al}_2\text{O}_3\text{─C}\) filter ceramics, because the coating is free of carbon.

A further increase in the carbon concentration in the \(\text{Al}_2\text{O}_3\text{─C}\) coating leads to a stronger development of the CO gas, which can be a reason for the observed flaking of the amorphous layer in the sample containing 30 mass\% C in \(\text{Al}_2\text{O}_3\text{─C}\) (Figure 3a). The amount of the developed CO gas, which was determined semi-quantitatively as the pressure obtained from the pressure measuring system in the SPS device and integrated over the process time, increased with increasing carbon content in the functional coatings. This result confirms the observations from the study by Schmidt et al.\[9\] The reaction layer is amorphous (Figure 3b) and consists mainly of O and Fe. The concentrations of Al and Si are lower than in the samples with lower carbon contents in the \(\text{Al}_2\text{O}_3\text{─C}\) coating. A low concentration of Al and Si reduces the melting temperature of the iron oxides. Thus, it is not sure, if the amorphous layer was present in a solid state also at 1600 °C. The wavy form of the interface between the Fe-rich part of the amorphous layer and the cavity that is visible at the upper edge of Figure 3a,c is a possible indicator of the solid–liquid transition with increasing Fe and decreasing Al content.

Still, also this amorphous layer seems to be active in attaching nonmetallic inclusions. An example is shown in Figure 3a, where a MnS particle is fixed to the surface of the amorphous layer. MnS are typical inclusions in the 42CrMo4 steel.\[27,33,34\] As the presence of carbon accelerates the reduction of \(\text{Al}_2\text{O}_3\) to Al by iron from molten steel,\[23\] this sample illustrates nicely the early stages of the secondary corundum formation. The secondary corundum forms in form of platelets (upper part of

![Figure 2](a) TEM micrograph of an interlayer formed between solidified steel 42CrMo4 and an α-\text{Al}_2\text{O}_3 coating with 4 mass\% C. The reaction experiment was conducted in SPS apparatus at the dwell time of 1 min at 1600 °C. b) SAED pattern of the interface layer. c) SAED of an α-Fe particle embedded in the amorphous layer.

![Figure 2](b) Amorphous layer

![Figure 2](c) 2 1 1 nm
Figure 3a) TEM micrograph of an interlayer formed between solidified steel 42CrMo4 and an α-Al2O3 coating with 30 mass% C. The layer was partly detached from the Al2O3–C coating due to a strong development of carbon oxide. The reaction experiment was carried out in SPS apparatus at the dwell time of 1 min at 1600 °C. b) SAED pattern of the interface layer. Panels on the right-hand side show the EDX distribution maps for Al, Fe, Mn, and O.

Figure 4a) TEM micrograph of an interface layer formed between solidified steel 42CrMo4 and a carbon-free functional corundum coating. The reaction experiment was conducted in a steel-casting simulator. The immersion time was 2 min at (1600 °C. b) SAED pattern of the interface layer.

3.2. Atomic Ordering in the Fe–Si–Al–O Interlayers

Although the reaction layers were preliminarily classified as amorphous based on the results of SAED (Figure 1b, 2b, and 3b), one can see small differences in individual SAED patterns, which can be related to ongoing crystallization. To promote the crystallization process, a sample containing carbon-free Al2O3 as functional coating was exposed to the 42CrMo4 melt for 2 min at 1600 °C. The experiment was carried out as an immersion test in a steel casting simulator. In this sample, a reaction layer developed as well (Figure 4a). It contained 55–60 at% of oxygen, about 40 at% of iron, small amounts of Si, and traces of Al. The SAED analysis revealed some crystalline features like weak diffraction spots and diffraction rings (Figure 4b), which were already expected from the diffraction contrast visible in Figure 4a.

For identification of the crystalline phases, which may form in the interlayer of this sample, the SAED pattern from Figure 4b was integrated in azimuthal direction. The diffracted intensities were corrected for the intensity factors depending on the diffraction angle and plotted as a function of the reciprocal interplanar spacing in Figure 5 (diffraction pattern at the bottom). Possible nanocrystalline phases present in the interlayer are a face-centered cubic (FCC) phase with the lattice parameter $a \approx 0.43$ nm, a spinel phase with the lattice parameter $a \approx 0.81$ nm and a garnet with the lattice parameter $a \approx 1.15$ nm. The coexistence of garnet and spinel structures in the quaternary Fe–Al–Si–O system was described in the study by Woodland and O’Neill.[35] The peak located at $\approx 6.7$ nm$^{-1}$ (marked by # in Figure 5), which corresponds to the positions of the weak, equidistantly spaced diffraction spots in Figure 4b, can be assigned to the diffraction line 220 of the FCC phase with the lattice parameter $a \approx 0.43$ nm. The spots stem from a larger crystallite, which was oriented with a direction {111} parallel to the direction of the primary electron beam.

The FCC phase can be assigned to wuestite (FeO, space group Fm3m, $a = 0.43$ nm).[36] Most prospective garnet phase is $Fe_3Al_2(SiO_4)_3$ with the space group $Ia3d$ and the lattice parameter $a = 1.152$ nm.[35] An unambiguous identification of the spinel phase is not possible, because the elements found in
the interlayers (Fe, O, Si, and Al) create several spinel phases with the space group \( Fd\overline{3}m \). The most prominent examples are \( \gamma \)-alumina, \( a = 0.791 \) nm, [37] hercynite, \( a = 0.816 \) nm, [38] magnetite, \( a = 0.840 \) nm [40] and a certain type of faujasite, \( Al_{1.22}(Al_{1.74}Si_{8.94}O_{22.32}) \), with the lattice parameter \( a/C25 = 2.47 \) nm [41]. As the spinel with the lattice parameter about \( 0.8 \) nm can accommodate different elements [42], including Fe, O, Si, and Al that were detected using EDX, the size of its elementary cell can vary in a broad range. Thus, the lattice parameter alone cannot be used for a direct identification of the chemical composition. Even the faujasite cannot be distinguished easily from the spinel phases, in particular, in a nanocrystalline form. As the lattice parameter of faujasite is approximately three times larger than the lattice parameters of the spinel phases, its diffraction pattern resembles the diffraction pattern of spinel, especially if faujasite is present in a strongly disordered form.

In the SAED patterns of the interlayers from samples that were brought in contact with the steel melt for 1 min at 1600 °C, the nanocrystalline features are much less developed than in the sample, which reacted with the molten steel for 2 min at the same temperature (Figure 5). This lower degree of crystallization can be a direct consequence of a shorter crystallization time. However, it should be mentioned that the sample, which experienced the longer reaction time, was produced by immersion test in a steel casting simulator. Primarily, the casting simulator is able to generate higher heating and cooling rates. Still, a much more important difference between the reaction experiments in SPS and in the casting simulator is that the filter ceramic was rotated in the steel melt during the immersion in the casting simulator [9]. Thus, the diffusivity of the elements was superimposed by the melt flow, which alters the proportions between the local concentrations of the elements involved in the reaction process.

### 3.3. Transformation of the Amorphous Layer

It was shown above that the reaction layer grows at the interfaces between the functionalized surface of the filter ceramics and the steel melt and that the formation of the reaction layer is preceded by the reduction of \( Al_{2}O_{3} \), which requires carbon as catalyst. The consequences of these chemical reactions are shown on the mesoscopic scale in Figure 6. In the carbon-free \( Al_{2}O_{3} \) coating, a carbon-depleted zone develops in the \( Al_{2}O_{3} - C \) filter ceramic, which is known from literature [17,22,27,43]. This was verified by the presence of droplets (bright spots in Figure 6a) containing mainly Fe, Cr, and Mo. This observation also confirms that the main body

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**Figure 5.** Diffraeted intensities obtained by integrating the SAEDs patterns from Figure 1b, 2b, 3b, and 4b in the azimuthal direction and plotted versus the reciprocal lattice spacing, calculated according to \( d/C25 = 1/d = \sqrt{h^2 + k^2 + l^2} / a \) for the respective lattice parameter \( a \) and the diffraction indices \( hkl \). Theoretical peak positions and the diffracted intensities are shown in a bar chart with differently shaded bars at the bottom of the figure for a spinel structure with a lattice parameter of about 0.81 nm, for FCC wuestite with a lattice parameter of about 0.43 nm and a garnet phase with a lattice parameter of about 1.15 nm. The diffracted intensities were calculated using kinematical diffraction theory assuming random orientation of crystallites.

**Figure 6.** SEM micrographs of functionalized \( Al_{2}O_{3} - C \) filters that were exposed to molten steel 42CrMo4 in SPS apparatus at 1600 °C for 1 min. The functional coatings consist of a) corundum without carbon, b) \( Al_{2}O_{3} - C \) with 4 mass% C, and c) \( Al_{2}O_{3} - C \) with 30 mass% C.
of the Al₂O₃—C filter ceramics is a source of carbon for the alumina reduction, when a porous carbon-free Al₂O₃ functional coating is used. Another source of carbon is, of course, the carbon present in the steel (≈0.4 mass%, see Table 2).

Underneath the functional Al₂O₃ coating containing 4 mass% carbon, the main body of the Al₂O₃—C filter ceramics is less decarburized (Figure 6b), because the carbon required for the Al₂O₃ reduction is obtained already from the functional coating. The uncoated substrate ceramics (corundum with 30 mass% C) experienced the most significant attack by the steel melt (Figure 6c). The steel penetrated into Al₂O₃—C up to a thickness of ≈40 μm. In contrast to the initially porous structure of the very fine-grained Al₂O₃—C ceramics (cf. unaltered Al₂O₃—C in the left part of Figure 6c), the corundum grains, which are in contact with the solidified steel, are significantly larger and form an almost completely dense, closely connected network.

An increase in the reaction time to 30 min led to a further densification of the uppermost layer, which is in contact with the solidified steel (Figure 7). Using SEM/EBSD (Figure 8), it was shown that this layer consists of almost equiaxed corundum crystallites having a size below 5 μm. The SEM/EBSD measurements were carried out between two adjacent filter struts, which were penetrated by molten steel (Figure 8). The distribution of corundum and solidified steel (α-ferrite) is shown in Figure 8b, the grain orientations of α-ferrite in Figure 8c, and the grain orientations of corundum in Figure 8d.

The equiaxed corundum crystallites are randomly oriented (Figure 8d) and smaller than the corundum crystallites in the original Al₂O₃—C coating (cf. Figure 6a,b). The decrease in the crystallite size is caused by the reduction of Al₂O₃ in the Al₂O₃—C coating and by its partial dissolution. The original pores and new cavities are filled by the oxide layer and by the products of the alumina reduction. The originally amorphous nature of the oxide layer facilitates the accommodation of the elements involved in the decomposition of Al₂O₃ (except carbon) and silicon from the steel. With proceeding crystallization of the oxides, however, the reaction layer expels iron and the alloying elements from the steel, and forms dense Al₂O₃ layer with a thickness of only few micrometers, which is much thinner than the filter struts (≈500 μm). Still, when the new Al₂O₃ coating becomes compact, it serves as a diffusion barrier for carbon from the main body of the Al₂O₃—C filter ceramics and for iron from the molten steel. Also, the paths to the source of carbon from the functional Al₂O₃—C coating are disrupted, because the pores in the functional coating are closed. The carbon involved in the Al₂O₃ reduction reacts with oxygen, leaves partly the reaction zone in form of gaseous CO and is not available for further reaction.[23] The consequences of these processes are a deceleration of the further reduction of Al₂O₃ and a cessation of the reaction layer formation.

3.4. Formation of Corundum Platelets on the Densified Filter Surface

In addition to the dense layer, which formed in all three Al₂O₃(-C) coatings under study (cf. Figure 7a–c), a significant amount of corundum platelets was observed in sample Al₂O₃—C with 4 mass% C (Figure 7b). In this sample, the platelets fully covered the surface of the filter struts and grew up to 20 μm into the former steel melt (Figure 9). To disclose the details about the formation of the corundum platelets, the SEM/EBSD measurements from Figure 8 were used again. The orientation EBSD
map (Figure 8d) shows that the platelets are differently oriented α-Al2O3 single crystals, which do not have a clear orientation relationship to the dense Al2O3 layer. The single-crystalline nature of the individual platelets is confirmed by their uniform orientation. The analysis of the observed orientations of the platelets (Figure 8d) revealed that their long sides have almost never the orientation {001}. Instead, the long sides of the platelets have frequently the orientations between {210} and {120}, which are perpendicular reciprocal space directions to the {001} direction. This means that the corundum platelets grow preferentially along the basal planes {001}, whereas their growth along the [001] direction is limited. Some Al2O3 platelets are attached to the compact corundum layer, whereas some of them grow in the metallic melt (Figure 8 and 9).

The Al2O3 platelets were observed mainly in the sample coated with the Al2O3-C functional coating containing 4 mass% C. This finding illustrates the interplay of the elements involved in the reaction between Al2O3, liquid iron, and carbon. As Al2O3 is reduced by liquid iron, only if carbon is present[23] the Al2O3 reduction is stopped, if the supply of carbon from the main body of the Al2O3-C filter is interrupted, e.g., by the compact Al2O3 layer. In such a case, the only source of carbon is the steel melt. However, this carbon reacts concurrently with oxygen to CO and leaves the reaction zone in gaseous form. Without carbon, remaining oxygen reacts with aluminum solved in the melt to Al2O3. Still, this reaction is slower than the analogous reaction occurring during the growth of the compact Al2O3 layer, because the local concentrations of aluminum and oxygen in the steel melt are lower than the concentrations of these elements in the vicinity of the carbon sources. Thus in the steel melt, the Al2O3 grows in form of thin platelets rather than in a compact form.

3.5. Effect of Amorphous Layer on the Formation of Dense Al2O3 and Al2O3 Platelets

To be able to explain the interplay between the crystallization of the originally amorphous layer, the formation of the compact
Al$_2$O$_3$ layer and the growth of the Al$_2$O$_3$ platelets, TEM micrographs and SAED patterns were taken at the interface between the compact Al$_2$O$_3$ layer and the Al$_2$O$_3$ platelets (Figure 10a), where a distinct interlayer between these two counterparts was identified (Figure 10b). These experiments were carried out with the sample coated with Al$_2$O$_3$–C containing 4 mass% C, which was in contact with molten steel for 30 min at 1600 °C. After this reaction time, the interlayer was crystalline—in contrast to amorphous interlayers that were found in the short-time reaction samples—and possessed the same crystallographic orientation like the corundum in the original Al$_2$O$_3$–C coating (cf. Figure 10c,d). This result illustrates the role of the local epitaxy in the crystallization of the former amorphous oxides.

Whereas the compact Al$_2$O$_3$ layer, which stems from aluminum and oxygen dissolved directly in the reaction zone, crystallizes with a pronounced orientation to the original functionalized filter surface (Figure 10b–d), a clear orientation relationship between the Al$_2$O$_3$ platelets and the compact Al$_2$O$_3$ layer is not apparent (Figure 10c–e). The reasons for this finding are different formation times and different formation mechanisms of the compact Al$_2$O$_3$ layer and the Al$_2$O$_3$ platelets. Whereas the compact Al$_2$O$_3$ layer crystallizes directly on a crystalline Al$_2$O$_3$ template, which is the functionalized surface of the metal melt filter, the Al$_2$O$_3$ platelets develop in the melt. The Al$_2$O$_3$ platelets are possibly attracted to the interlayer. However, if the interlayer is not fully crystallized, when the contact between the platelet and the interlayer is established, it cannot act as a docking site for an epitaxial growth.

4. Discussion

The experimental results confirmed the reaction process between alumina, liquid iron, and carbon proposed by Zienert et al. and illustrated the influence of the amount of carbon in functional Al$_2$O$_3$–C coating on the reaction process. It was shown that iron, aluminum, and oxygen, which are the direct products of the carbothermic reaction, form first a thin amorphous layer on the interface between the molten steel and the functionalized filter surface. This amorphous layer attracts impurities and alloying elements from molten 42CrMo4 steel, in particular silicon. This phenomenon is of a great practical importance. The main constituents of the amorphous layer are iron aluminum silicon oxides, which crystallize to nanocrystalline wuestite and spinel and garnet-like structures at longer reaction times. In this way, a compact layer on the surface of the functionalized filter is formed, which close the pores in the functional coating and interrupts the paths to the source of carbon. Concurrently, carbon reacts with free oxygen to CO and is missing as catalyst of the further reduction of Al$_2$O$_3$. When the carbon content is too low to facilitate the Al$_2$O$_3$ reduction, aluminum and oxygen dissolved in the molten steel form Al$_2$O$_3$ in form of thin platelets. Consequently, the reaction of oxygen with carbon and aluminum reduces the oxygen content in the steel. As steel powder was used in these experiments, the initial oxygen content was quite high (about 0.3 at%). After the reaction with the Al$_2$O$_3$–C filter, the oxygen content was reduced to about 0.01 at%. A similar deoxidation of the melt was observed in real filtration processes, in which the 42CrMo4 steel was filtered by Al$_2$O$_3$–C filter coatings.

After a long reaction time, the nanocrystalline oxides transform to corundum. A possible transient phase is metastable γ-Al$_2$O$_3$, which possesses a spinel-like crystal structure containing highly mobile structural vacancies. Their presence facilitates a fast exchange of metallic species, which is needed to remove iron and/or silicon from the spinel-like structures. As the amorphous layer grows on corundum, which is a part of the functionalized filter surface, it adopts the crystal structure of this substrate during the crystallization. The epitaxial growth plays an important role in this crystallization process. In contrast to corundum that crystallizes on the surface and in the pores of the former functional coating, the corundum that stems from aluminum and oxygen dissolved in the steel melt, crystallizes in form of platelets. These platelets do not have any obvious orientation relationship to the filter surface, because they possess no or a very local contact with the filter surface or they adhered to the filter surface, when it was covered by an amorphous interlayer.

Although the amount of aluminum, oxygen, and carbon in the molten steel seems to be always reduced by the reactions between

![Figure 10](image-url)
these three elements, it must be noted that the amount of accessible carbon from the functionalized metal melt filter can influence the purity of the steel essentially. If the amount of carbon is too low, the formation of the active amorphous layer is impeded. Furthermore, the carbon from the steel melt is spent as the catalyzer of the Al₂O₃ reduction. Thus, the carbon concentration in the steel is decreased. If the amount of carbon in the functionalized filter is too high, then the dissolved oxygen, which stems either from the steel or from reduced Al₂O₃, reacts with carbon. This leads to an enhanced production of CO and to the alloying of the steel with aluminum.

5. Conclusions

The experimental results confirmed that Al₂O₃-based functional coatings covering the surface of the metal melt filters are reduced by liquid iron, if carbon is present as a catalyzer of this reaction. The products of the Al₂O₃ reduction are iron oxides containing Al and Si (and other alloying element from the steel), and CO gas. On a short-time scale, these oxides form a thin amorphous layer, which can attract and attach nonmetallic inclusions from the steel melt. However, this layer serves as a barrier for the carbon supply from the functionalized metal melt filter. At longer reaction times, the amorphous layer crystallizes and forms dense corundum layer, which is impermeable for further carbon diffusion from the Al₂O₃–C filter and for the iron from the melt. Consequently, the reduction of Al₂O₃ from the functionalized filter is stopped.

The reduction of Al₂O₃ present in the functionalized filter surface and the formation of secondary corundum on the former filter surface are two concurrent reactions. Both occur in contact with liquid iron. However, as the Al₂O₃ reduction is facilitated by the presence of carbon, whereas the secondary corundum forms preferentially when carbon is absent, the local concentration of carbon is a crucial factor in influencing the rate of the individual reaction. The supply of carbon is controlled by the concentration of carbon in the functionalized filter and in the steel melt, and affected by the rate of the CO formation. Additional important factors influencing the reaction process are the morphology of the Al₂O₃–C filters, their porosity, and the morphology of the secondary corundum. From this point of view, the secondary corundum can be reduced in the same way like the primary corundum from the metal melt filter, if it forms small and separated crystallites that can be soaked by liquid iron, and if the local concentration of carbon is sufficiently high. On the contrary, large and compact crystallites of secondary corundum surrounded by carbon-depleted steel melt stay stable. They act as efficient barrier for carbon diffusion and iron penetration, and as docking centers for adhesion of plate-like Al₂O₃ crystallites stemming from the reaction between aluminum and oxygen dissolved in carbon-depleted steel melt.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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42CrMo4 steels, electron microscopy, interfacial reactions, reactive metal melt filters, spark plasma sintering

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