Impact of rim zone modifications on the surface finishing of ferritic–pearlitic 42CrMo4 using electrochemical machining

Daniela Zander | Alexander Schupp | Stefanie Mergenthaler | René D. Pütz | Christoph Altenbach

Division of Materials Science and Engineering, Foundry Institute, Chair of Corrosion and Corrosion Protection, RWTH Aachen University, Aachen, Germany

Correspondence
Daniela Zander, Division of Materials Science and Engineering, Foundry Institute, Chair of Corrosion and Corrosion Protection, RWTH Aachen University, 52072 Aachen, Germany. Email: d.zander@gi.rwth-aachen.de

Funding information
Deutsche Forschungsgemeinschaft, Grant/Award Number: 223500200-TRR 136

Abstract
The efficiency of material removal using electrochemical machining (ECM) is highly dependent on the initial rim zone modifications of the material to be processed. The influence of the rim zone modifications, such as topography and microstructure, on ECM, is investigated on ferritic–pearlitic 42CrMo4 steel by experiment and simulation. 42CrMo4 steel in two different pre-machining states—ground and electric discharge machined (EDM)—is subjected to a subsequent surface finishing by ECM in sodium nitrate solution. Before and after ECM, the topography and microstructure are examined using scanning electron microscopy, X-ray diffractometer, and topography analysis methods. The electrochemical properties of the material are determined by potentiodynamic polarization. The efficiency of surface finishing by ECM is quantified by mass spectroscopic analysis (inductively coupled plasma mass spectrometry) of the process electrolyte and related to the rim zone modifications by simulation. The results reveal that the efficiency of material removal during ECM is higher for EDM than for ground 42CrMo4. This is attributed to an increased roughness of EDM 42CrMo4 and to the unfavorable electrochemical properties of the cementite phase in ground 42CrMo4.

KEYWORDS
42CrMo4 steel, electrochemical machining, electrochemical simulation, rim zone modifications, surface finishing

1 | INTRODUCTION

Electrochemical machining (ECM) of metals is a widely used process in the industry for manufacturing difficult to machine materials\(^{[1,2]}\) and surface finishing.\(^{[3,4]}\) It is based on the electrochemical dissolution of metals in a conductive electrolyte by applying an external, anodic potential between the workpiece and a cathode. DC voltages of around 10–25 V and current densities of up to 200 A cm\(^{-2}\) are common for ECM.\(^{[5]}\) One important advantage of ECM is the ability to machine materials without the input of mechanical or thermal loads. This makes it possible to machine materials almost without negative rim zone changes or to remove already existing undesirable rim zone
modifications obtained by previous thermal or mechanical manufacturing processes. The ECM process is therefore particularly suitable for the surface finishing of materials for which a good surface quality is required.

The steel 42CrMo4, for example, which is mostly used for components subjected to high mechanical stresses like crankshafts, [6,7] is usually machined with abrasive or thermal (e.g., EDM) removal methods. However, this leads to undesired changes in the rim zone, such as the generation of residual stresses, changes in the microstructure, partial melting, or the formation of heat-affected zones, which might have a negative effect on the functionality of the component. [8-10] In this case, the ECM process provides a high potential for post-processing components, manufactured by mechanical or thermal methods, to remove undesirable rim zone modifications and improve surface integrity.

The electrolytic condition describes one major processing parameter for ECM. It was reported that concentrated salt solutions are suitable electrolytes for ECM processing of iron and steel due to their good conductivity. Mao [11,12] studied the transpassive dissolution of mild steel in the electrolytes NaCl, NaClO4, NaClO3, and NaNO3. It was proven that the efficiency of ECM is higher in chloride-containing electrolytes in comparison to chloride-free sodium nitrate electrolyte. This was attributed to the formation of a dense, electrically conductive oxide layer in sodium nitrate, which leads to the predominant evolution of oxygen on the oxide surface and results in a reduced efficiency during the ECM process. However, Hoare et al. [13] and Chin et al. [14] recommend that ECM machining of mild steels in sodium nitrate solution is preferable because sodium nitrate solution has a passivating effect on steel and, unlike other common electrolyte systems, such as NaCl or NaClO3, does not favor the formation of pitting corrosion.

Therefore, the study on the overall electrochemical properties of 42CrMo4 steel in sodium nitrate electrolytes is of high interest and was investigated in several studies. According to Klocke et al., [24,25] the corrosion potential of 42CrMo4 steel in sodium nitrate solution (36°C) was about −0.5 V SHE. One distinct current density maximum associated with the formation of a passive layer, and followed by a passive and a transpassive region at about 1.5 V SHE was observed. Mehrafsun et al. confirmed these results. Additional investigations on the influence of temperature on the passivation behavior for 42CrMo4 steel in 2.5 M sodium nitrate solution at temperatures between 20°C and 50°C revealed an increase of the active and transpassive current density as well as a less pronounced passive region with increasing electrolyte temperature. [16]

Typically, the ECM process is performed at high potentials and anodic current densities in the transpassive region in which two concurring reactions take place: (a) metal dissolution via the intermediate step of an oxide layer formation and (b) the development of oxygen. Lohrengel et al., [17,18] Rosenkranz et al., [19] and Münninghoff [20] established a correlation between the current density and the efficiency of the ECM process. For iron in sodium nitrate solution, it was reported that oxygen evolution is the dominant reaction in the transpassive region at low current densities of <10 A cm⁻². In contrast, at higher current densities, the anodic metal dissolution becomes the predominant reaction. This means that proportionally more energy flows into the dissolution of iron than into the undesired formation of oxygen. Consequently, the efficiency of the ECM process increases with increasing current density. Lohrengel et al. [21] reported an almost linear increase of the current density with the potential for iron in sodium nitrate solution in the transpassive region.

In addition, Saubetin et al. [22] and Gurumurthy et al. [23] determined through experiments and theoretical FEM simulations that the ECM process leads to a smoothening of surfaces. Saubetin et al. attribute this to the fact that the distance between the protruding areas of the surface and the cathode is smaller than the distance between the other areas of the material surface and the cathode. The losses due to the relatively low electrical conductivity of the electrolyte are therefore lower in the protruding areas, which promotes the dissolution of the material there.

Klocke et al. [24,25] have investigated the effect of ECM on the microstructure of ferritic–pearlitic 42CrMo4 steel in 2.5 M sodium nitrate solution. Selective dissolution of the steel with a preferred dissolution of the electrochemically less noble ferrite phase in contrast to the cementite phase was proven. According to Klink, [26] Harst, [27] as well as Bergs and Harst, [28] this selective dissolution is directly connected to the applied electric field. However, up to now, there are hardly any investigations on the impact of rim zone modifications obtained by previous thermal or mechanical manufacturing processes, such as grinding and EDM, on the efficiency of the ECM surface finishing process. Therefore, this study focuses on the influence of rim zone modifications, such as topography and microstructure, on the electrochemical machinability by ECM.

2  | MATERIALS AND METHODS

2.1  | Materials

The influence of the rim zone modifications on the subsequent surface finishing by ECM is investigated on two different preprocessed surfaces: ground and electric
discharge machined (EDM) 42CrMo4. The main metallic alloying elements of heat-treatable 42CrMo4 (AISI4140) steel are chromium, manganese, and molybdenum. The complete chemical composition is given in Table 1.

42CrMo4 was subjected to a heat treatment to achieve a ferritic–pearlitic microstructure. Therefore, the ingot material was austenitized in a vacuum furnace at 850°C for 2 h, followed by cooling down to room temperature in the furnace at a rate of 1.7 K min⁻¹. After heat treatment, the ingots were cut into cylinders with a height of 6 mm and a diameter of 10 mm. The head surface of the cylinders is being premachined either by grinding or EDM using a half-automatic grinding and polishing machine type Saphir 550 from ATM Qness GmbH and a GF AgieCharmilles FORM 2000 VHP, respectively. The process parameters of grinding (FP-GRI) and EDM (FP-EDM) are shown in Table 2.

### 2.2 Methods

#### 2.2.1 Analysis of bulk material

To characterize the bulk microstructure, the material was polished up to 0.25 μm using a diamond suspension. Prior examination of the microstructure by using an optical light microscope type Zeiss Apollo, the specimens were subjected to an etching process with 2% Nital solution to visualize the different phases, such as ferrite and pearlite. A quantitative proportion measurement of the phases was conducted using ImageJ software. Furthermore, Vickers hardness testing of the bulk microstructure was performed using a Buehler Micromet 5100 Series with a test load of 1.961 N (HV 0.2).

#### 2.2.2 Microstructure and topography of ground and EDM 42CrMo4 rim zones

Phase analysis of ground and EDM rim zones before and after surface finishing by ECM was conducted using a Panalytical Empyrean X-ray diffractometer (XRD) with Co-Kα radiation (40 kV, 40 mA). The Panalytical High-score Plus software with ICDD and ICSD databases were used to determine the different phases.

Additionally, the microstructure and chemical composition of ground and EDM rim zones were characterized by scanning electron microscopy (SEM) using a Zeiss Ultra 55, equipped with an Oxford energy-dispersive X-ray spectroscopy (EDX) facility before and after surface finishing by ECM. The acceleration voltage was adjusted to 15 kV and a working distance of approximately 10 mm was used. Beyond this, cross sections of the respective rim zones were subjected to etching with a solution made of 2 g CuCl₂, 40 ml ethanol, and 40 ml concentrated hydrochloric acid for 10 s at room temperature and subsequently analyzed in terms of characterizing the rim zone of ground and EDM 42CrMo4 before and after surface finishing by ECM using a Zeiss Supra 55 VP scanning electron microscope.

The topography of the machined surfaces was geometricaly characterized according to DIN EN ISO 16610-21 and DIN EN ISO 16610-31 by using a Marsurf XC. Roughness parameters, such as average roughness value (Rₐ), average peak-to-valley height (Rₛ), and maximum peak-to-valley height (Rₘₐₓ), of at least three samples per

### Table 1 Chemical composition of 42CrMo4 steel

| Element | wt% | at% |
|---------|-----|-----|
| C       | 0.43 | 1.96 |
| Si      | 0.26 | 0.51 |
| Mn      | 0.74 | 0.74 |
| P       | 0.01 | 0.018 |
| S       | <0.001 | <0.002 |
| Cr      | 1.09 | 1.15 |
| Mo      | 0.25 | 0.14 |
| Fe      | Bal. | Bal. |

### Table 2 Process parameters of grinding and EDM

| Grinding          | Electric discharge machining (EDM) |
|-------------------|-----------------------------------|
| Technique         | Rotating grinding wheel            | Technique                          |
| Fluid             | Water                             | Fluid                              |
| Rotation speed    | 150 rpm                           | Rotation speed                     |
| Grinding pressure | 15 N                              | Grinding pressure                 |
| Abrasive paper    | SiC                               | Abrasive paper                     |
| Grain size of abrasive paper | 180–320–500–1000 | Grain size of abrasive paper       |
| Time per grinding step | 2–3 min                           | Time per grinding step             |
surface condition were measured via the profile method and evaluated with the MarWin 9.0 evaluation program. Furthermore, the developed interfacial area ratio (Sdr) was calculated from roughness profiles, obtained by using a Tosca-400 atomic force microscope (AFM) from Anton Paar. The Sdr was calculated according to DIN EN ISO 25178-2\(^2\) and used to recalculate the effective surface participating in electrochemical reactions during potentiodynamic polarization experiments and surface finishing by ECM. Additionally, three-dimensional surface pictures were conducted by a laser scanning microscope VK 9700K from Keyence GmbH.

### 2.2.3 Electrochemical properties

The electrochemical properties of ground and EDM 42CrMo4 were characterized by potentiodynamic polarization experiments according to DIN EN ISO 17475\(^3\) and ASTM G5\(^4\) with a larger scan rate of 0.5 mV s\(^{-1}\). A three-electrode setup, consisting of a saturated calomel electrode (SCE), a platinum wire as a counter electrode, and the respective machined surface as the working electrode was connected to a Gamry Instruments Reference 600 potentiostat. The machined surfaces were exposed to naturally aerated 2.5 M sodium nitrate solution at a pH between 8.4 and 8.6, with a conductivity of 160 mS cm\(^{-1}\) and a temperature of 36°C, which are standard ECM machining conditions.\(^5\) Initially, the open-circuit potential (OCP) of the specimens was measured for a duration of 60 min. Subsequently, potentiodynamic polarization was performed in the range of –1.5 to 2.3 V\(_{\text{SCE}}\). In addition, potentiostatic polarization was performed using the same experimental setup on ground 42CrMo4 at 2 V\(_{\text{SCE}}\).

### 2.2.4 Surface finishing by ECM

To study the influence of rim zone modifications obtained by grinding and EDM on the surface finishing by ECM, electrochemical dissolution was performed in the transpassive region of ground and EDM 42CrMo4 at an external DC voltage of 15 V for 10 s in 0.2 L of a 2.5 M NaNO\(_3\) solution at 36°C. The sample was interconnected as a working electrode (anode) and a platinum sheet as a counter electrode (cathode). The gap width between the anode and the cathode was adjusted to 1.5 mm.

The change in concentration of metal ions in the electrolyte due to surface finishing by ECM was measured using a PerkinElmer NexION 2000 mass spectrometer with inductively coupled plasma (ICP-MS). Before the measurement, the electrolyte was diluted 1:50 with 2% nitric acid to ensure that all metallic components are in solution. ICP-MS measurements were performed on the electrolyte before and after ECM. The composition of the electrolyte after ECM enables statements about the effectiveness and the mechanism of material removal. The efficiency of the ECM process can be estimated by using Faraday’s law in the following equation:

\[
m_F = \frac{MQ}{zF}.
\]

Here, \(m_F\) is the mass of the dissolved metal ions, \(M\) the molar mass, \(Q\) the charge transferred, \(z\) the charge number of the ions formed, and \(F\) the Faraday constant. The process efficiency \(\eta\) can be calculated by comparing the mass of dissolved ions measured by ICP-MS (\(m_{\text{ICP-MS}}\)) and the mass of ions calculated from the transferred charge \(Q\) by using Faraday’s law (\(m_F\)) according to the following equation:

\[
\eta = \frac{m_{\text{ICP-MS}}}{m_F} \times 100\%.
\]

### 2.2.5 Simulation

The electrochemical dissolution of ground and EDM 42CrMo4 during ECM surface finishing was simulated using the finite element method to support the experiments. The software COMSOL Multiphysics was used for this purpose. For the calculation, a simplified two-dimensional numerical model was used that consists of an anode, cathode, and an intermediate electrolyte. A simulated voltage was applied between the anode and the cathode resulting in electric current flow. The average current density was adapted to the current densities measured during the experiments (Table 3). The material removal at the anode was simulated using deforming geometries. The anodic surface is movable to show the dissolution of the material. The speed of this movement (mass removal \(m_r\)) depends on the current density \((i)\) via a proportionality factor \(K\) as

\[
m_r = -K \times i.
\]

\(K\) depends on the phase. For austenite and ferrite, this factor can easily be calculated using Faraday’s law via the molar mass \((M)\) and density \((\rho)\) in the following equation:

\[
K = \frac{M}{\rho z F}.
\]

It is known from previous simulations by Harst\(^2\) that cementite and ferrite in ferritic–pearlitic 42CrMo4 steel dissolve at the same rate in the ECM process if the current density at the cementite phase is greater by a factor of 1.392 compared with the ferrite phase. This factor was used to calculate the value of \(K_{\text{cementite}}\) (see Table 4). During the real ECM process, however, only a
small portion of the transferred charge is ever used for metal dissolution. The rest is lost, for example, through the formation of oxygen or through the formation of oxidic layers on the anodic surface. These charge losses must be taken into account for the simulation. Therefore, the experimentally determined charge efficiency (Table 5) is multiplied by the coefficient $K$. 

Two different types of anodes have been simulated: an anode with a smooth, ground surface and an anode with a rough EDM surface. Experimentally obtained roughness measurements and cross-sectional analysis of ground and EDM-machined samples were the basis for the description of the simulated roughness of ground and EDM surfaces. In addition, it was assumed for the simulations that ground surface consists of a pearlitic microstructure, containing ferritic and cementite lamellae, and the EDM surface of a completely austenitic microstructure.

### 3 RESULTS

#### 3.1 Microstructure and rim zone modifications of 42CrMo4 before surface finishing by ECM

Microstructural investigations of 42CrMo4 by optical light microscopy (OLM) revealed a ferritic–pearlitic microstructure (Figure 1). The quantitative determination of the phase fraction after etching in 2% Nital solution resulted in a pearlite proportion of $79 \pm 6\%$ compared with $21 \pm 6\%$ ferrite.

In addition, a Vickers hardness of $188 \pm 11$ HV 0.2 was obtained for the ferritic–pearlitic 42CrMo4. The results of the hardness measurements and the microstructure analysis agree well with the time-temperature conversion diagram of the material 42CrMo4.\[^{15}\]

To be able to explain the impact and differences between the rim zone modifications of ground and EDM 42CrMo4 on surface finishing by ECM, further microstructural and roughness investigations of the rim zone by X-ray diffraction, SEM, AFM, confocal microscope, and profile method were performed before ECM. Figure 2 shows the X-ray diffractograms of ground and electro-discharge machined specimens of ferritic–pearlitic 42CrMo4 before ECM. The ferritic phase ($\alpha$-Fe) was observed after both machining processes. In addition, the formation of the austenitic phase ($\gamma$-Fe) at the surface of EDM processed 42CrMo4 was observed, which is associated with the thermal impact on the surface during the EDM process. This was reported\[^{9}\] to lead to a change from a ferritic–pearlitic microstructure toward an austenitic microstructure in the rim zone and is in good agreement with the presented results.

SEM backscatter electron (BSE) cross-sectional images of ground and EDM 42CrMo4 are shown in Figure 3. Grinding leads to a flat surface with small grinding marks (Figure 3a), whereas the rim zone of EDM

### Table 3 Material removal of ground and EDM 42CrMo4 during surface finishing by ECM (10 s, 15 V) calculated by Faraday's law

|                | FP-GRI   | FP-EDM   |
|----------------|----------|----------|
| Current (A)    | $6.5 \pm 0.2$ | $6.4 \pm 0.4$ |
| Test duration (s) | 10       | 10       |
| Charge (C)     | $65 \pm 2$ | $64 \pm 4$ |
| Calculated material removal (mg) | $18.7 \pm 0.5$ | $18.4 \pm 1.1$ |
| Calculated thickness reduction (μm) | $11.5 \pm 0.3$ | $11.3 \pm 0.7$ |

Abbreviations: ECM, electrochemical machining; EDM, electrical discharge machining.

### Table 5 Material removal of ground and EDM 42CrMo4 during surface finishing by ECM (10 s, 15 V) measured by ICP-MS

|                | FP-GRI   | FP-EDM   |
|----------------|----------|----------|
| Material removal (mg) | $2.15 \pm 0.34$ | $3.50 \pm 0.06$ |
| Thickness reduction (μm) | $1.3 \pm 0.2$ | $2.2 \pm 0.1$ |
| ECM efficiency (%) | $11.5$ | $19.0$ |

Abbreviations: ECM, electrochemical machining; EDM, electrical discharge machining; ICP-MS, inductively coupled plasma mass spectrometry.

### Table 4 Parameters for the FEM simulation of surface finishing of 42CrMo4 by ECM

| Parameter  | Description                  | Value          |
|------------|------------------------------|----------------|
| $d$        | Distance between anode and cathode | $1.5$ mm       |
| $\sigma_{\text{electrolyte}}$ | Electric conductivity of the electrolyte | $16$ S m$^{-1}$ |
| $i_{\text{average}}$ | Average current density | $8$ A cm$^{-2}$ |
| $K_{\text{ferrite}}$ | Coefficient of proportionality ferrite | $2.45 \times 10^{-11}$ m$^3$ A$^{-1}$ s$^{-1}$ |
| $K_{\text{cementite}}$ | Coefficient of proportionality cementite | $1.76 \times 10^{-11}$ m$^3$ A$^{-1}$ s$^{-1}$ |
| $K_{\text{austenite}}$ | Coefficient of proportionality austenite | $2.45 \times 10^{-11}$ m$^3$ A$^{-1}$ s$^{-1}$ |

Abbreviation: ECM, electrochemical machining.
42CrMo4 reveals a wavelike, rough surface with regions of resolidified deposits (Figure 3b). The latter was associated with the formation of the austenitic phase during the EDM process, which is shown in Figure 3c after etching.

The different topographies observed by SEM were characterized by profile methods and AFM to obtain standard roughness parameters, such as \( R_a \), \( R_z \), \( R_{\text{max}} \), and \( \text{Sdr} \) (Table 6). Ground surfaces exhibit low roughness values that are comparable to polished surfaces. However, the roughness on EDM surfaces was significantly increased compared with ground 42CrMo4.

In addition, confocal microscopy investigations, displayed by three-dimensional roughness profiles, confirmed a smooth surface topography after grinding and the formation of grinding marks that are aligned in the grinding direction (Figure 4a). In contrast to this, the EDM surfaces (Figure 4b) exhibit a wavelike topography with brought craters. According to the SEM investigations of the cross-section, it is assumed that the thickness of the resolidified melt deposits varies between the deepest point of the craters and the areas between the craters.

### 3.2 Electrochemical characterization and surface finishing of 42CrMo4

Electrochemical potentiodynamic and potentiostatic investigations were performed to evaluate the influence of the different rim zone modifications on the electrochemical properties of 42CrMo4 in 2.5 M sodium nitrate solution. This should also allow conclusions on the impact of the rim zone modifications on the ECM process performed in sodium nitrate solution at transpassive potentials. Figure 5 illustrates the results of the potentiodynamic polarization experiments performed with ground and EDM surfaces of 42CrMo4. Table 7 reveals the electrochemical parameters obtained from potentiodynamic polarization.

In general, the cathodic branch already indicates an unstable passivating system, which is more pronounced for ground 42CrMo4 compared with the EDM 42CrMo4. With regard to the corrosion potential and the corrosion current density, an influence of the surface modification dependent on the machining process was recognized. It was seen that EDM significantly shifts the corrosion potential in the anodic direction. The difference between the corrosion potentials of ground and the EDM surfaces is 147 mV.

Both rim zone modifications reveal a distinctive activation area and a two-step passivation mechanism. The average passivation potential \( E_{\text{pp}} \) differs significantly between ground and EDM 42CrMo4. The correlated critical current density \( i_{\text{crit}} \) exhibits higher values for ground compared with EDM surfaces. Further, significant differences related to the two-step passivation mechanism were observed. In contrast to the EDM rim zone modification, ground 42CrMo4 surfaces show a
FIGURE 3  SEM-BSE cross-sectional images at the rim zone of (a) ground, (b) and (c) EDM 42CrMo4 before surface finishing via ECM. ECM, electrochemical machining; EDM, electrical discharge machining.

| Roughness values [µm] | Developed interfacial area ratio (µm) |
|-----------------------|--------------------------------------|
|                       | $R_a$  | $R_x$  | $R_{max}$ | Sdr |
| FP-GRI                | 0.036 ± 0.004 | 0.35 ± 0.05 | 0.46 ± 0.10 | 0.01 |
| FP-EDM                | 2.051 ± 0.207 | 12.89 ± 1.98 | 15.74 ± 3.44 | 0.08 |

Abbreviations: ECM, electrochemical machining; EDM, electrical discharge machining.

FIGURE 4  Roughness profile images of (a) ground and (b) EDM 42CrMo4 before surface finishing by ECM. ECM, electrochemical machining; EDM, electrical discharge machining [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 5  Potentiodynamic polarization curves of ground and EDM 42CrMo4 before surface finishing by ECM in naturally aerated 2.5 M sodium nitrate solution, determined at 36°C using a scan rate of 0.5 mV s$^{-1}$. ECM, electrochemical machining; EDM, electrical discharge machining [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 6  Roughness parameters of ground and EDM 42CrMo4 before surface finishing by ECM

| Roughness values [µm] | Developed interfacial area ratio (µm) |
|-----------------------|--------------------------------------|
|                       | $R_a$  | $R_x$  | $R_{max}$ | Sdr |
| FP-GRI                | 0.036 ± 0.004 | 0.35 ± 0.05 | 0.46 ± 0.10 | 0.01 |
| FP-EDM                | 2.051 ± 0.207 | 12.89 ± 1.98 | 15.74 ± 3.44 | 0.08 |

Abbreviations: ECM, electrochemical machining; EDM, electrical discharge machining.

TABLE 7  Average corrosion numbers of ground and EDM 42CrMo4 before surface finishing by ECM in naturally aerated 2.5 M sodium nitrate solution at 36°C

|                   | FP-GRI | FP-EDM |
|-------------------|--------|--------|
| $E_{corr}$ (V SCE) | 0.552 ± 0.010 | 0.405 ± 0.003 |
| $i_{corr}$ (mA cm$^{-2}$) | 0.037 ± 0.018 | 0.072 ± 0.044 |
| $E_{pp}$ (V SCE) | 0.166 ± 0.025 | 0.066 ± 0.048 |
| $i_{crit}$ (A cm$^{-2}$) | 0.171 ± 0.004 | 0.107 ± 0.006 |
| $i_{pass}(1)$ (mA cm$^{-2}$) | 0.276 ± 0.035 | 0.130 ± 0.011 |
| $i_{pass}(2)$ (mA cm$^{-2}$) | 0.461 ± 0.083 | 0.454 ± 0.281 |

Abbreviations: ECM, electrochemical machining; EDM, electrical discharge machining.
secondary anodic current density maximum at a potential of 0.9–1.2 V_{SCE}, followed by a short secondary passivation step. The EDM process results in a rim zone modification, which has no distinct secondary anodic current density maximum area but exhibits a step-like increase of the secondary passivation current densities \( i_{\text{pass,2}} \). In general, the passivation current densities are lower for the EDM process in comparison with ground surfaces.

The transpassive area, which is relevant for the ECM process, is dominated by the instability of the oxide, oxygen evolution, and material removal at higher voltages. The breakthrough potential determines the start of the transpassivation and occurs for both rim zone modifications at 1.4 V_{SCE}. Furthermore, a ternary passive region is visible for both surface states in the range of 1.6–1.8 V_{SCE}, which is more pronounced for ground 42CrMo4. At higher potentials of above 1.8 V_{SCE}, higher current densities for ground compared with EDM rim zones were measured. ICP-MS measurements of the electrolyte after potentiostatic polarization of ground 42CrMo4 at 2 V_{SCE} revealed that about 99% of the current density is caused by the formation of oxygen and only about 1% by the dissolution of iron and chromium. Therefore, it is assumed that the oxygen evolution in the transpassive area up to 2 V_{SCE} is dominant compared with the material dissolution. This indicates that at the same potential, more oxygen evolves on ground surfaces in comparison with the EDM surfaces. In addition, it was observed that chromium dissolution compared with iron dissolution is proportionately higher for chromium in the transpassive area.

However, to obtain a significant material removal by ECM, the surface finishing is typically performed at very high potentials between 15 and 20 V. This depends on the alloy, electrolyte, and temperature. Therefore, ground and EDM 42CrMo4 were exposed to an external potential of 15 V for 10 s leading to transpassive dissolution. During the electrochemical material removal, strong gas evolution was observed for both surface states. Additionally, the precipitation of a brownish solid from the electrolyte was observed. Due to the low solubility of iron in the sodium nitrate electrolyte, the precipitation of an iron hydroxide can be assumed. However, the amount of material removal was investigated on the one hand theoretically by Faraday’s law as well as experimentally by ICP-MS measurements of the electrolytic components, such as iron, chromium, molybdenum, and manganese. Therefore, the current flow between the surfaces and the platinum sheet was measured during the process. The results of these measurements, as well as the calculated charge, are listed in Table 3. Currents of about 6.5 A are present for ground as well as the EDM rim zones. This results in an almost constant current density of approximately 8 A cm\(^{-2}\) during the whole processing period.

Using Faraday’s law (Equation (1)), a theoretically possible material removal can be calculated from the results of the current flow measurements considering 100% efficiency of the process. For simplification, the calculation was carried out for iron only. The amount of the other alloying elements in the alloy is lower than 3 wt % and was neglected for the calculation. Considering the two different oxidation states of iron, such as Fe\(^{3+}\) and Fe\(^{2+}\), and the related efficiency of electron transfer, the maximum theoretically possible material removal was calculated with \( z = 2 \), resulting in very similar material removal of 18.7 mg for ground and 18.4 mg for EDM 42CrMo4. However, due to the observed additional oxygen evolution as well as the possibility of the formation of Fe\(^{2+}\), Fe\(^{3+}\), Cr\(^{3+}\), CrO\(_4^{2-}\) and the different oxidation states of Mo and Mn during ECM, typically the process efficiency is lower than 100%. Therefore, additional ICP-MS measurements of the electrolyte after 10 s at 15 V of ECM surface finishing were performed for the relevant alloying elements, such as iron, chromium, molybdenum, and manganese (Table 8). It was observed that surface machining by grinding compared with EDM reveals a lower dissolution of all alloying elements during the ECM finishing process. Comparing the Fe/Cr ratio within the alloy with that of the dissolved elements in the electrolyte, it was observed that a preferential chromium dissolution occurred during ECM (Table 8).

According to the obtained ICP-MS results, Table 5 shows the measured real material removal through the transpassive metal dissolution. In contrast to the calculated material removal (Table 3) and the assumed efficiency of 100%, significant differences in the material removal of the two rim zone modifications were observed. On the one hand, the efficiency of the ECM process, which was calculated by Equation (2), was only 11.5% for ground compared with 19% for EDM 42CrMo4. In addition, it was observed that the material removal of

| Abbreviations: ECM, electrochemical machining; EDM, electrical discharge machining; ICP-MS, inductively coupled plasma mass spectrometry. |

**TABLE 8** Results of ICP-MS measurements of ground and EDM 42CrMo4 after ECM at 15 V, 10 s

| Element | FP-GRI | FP-EDM |
|---------|--------|--------|
| Fe (mg) | 2.101 ± 0.330 | 3.419 ± 0.133 |
| Cr (mg) | 0.029 ± 0.011 | 0.044 ± 0.003 |
| Mn (mg) | 0.017 ± 0.003 | 0.031 ± 0.001 |
| Mo (mg) | 0.005 ± 0.001 | 0.008 ± 0.001 |
| Fe/Cr ratio (–) | 72 | 77 |
The removal of either ferritic–pearlitic or austenitic phases during ECM leads already after 10 s to microstructural changes of the rim zones. X-ray diffraction (Figure 6) especially reveals the removal of the austenitic phase that was obtained by EDM before ECM. It is assumed that mainly the ferritic–pearlitic phase is present after the ECM surface finishing of EDM 42CrMo4. Therefore, most of the austenitic phase is removed by ECM. The ground 42CrMo4 reflects no phase changes.

SEM backscatter electron (BSE) cross-sectional images of each surface state after the transpassive dissolution at 15 V for 10 s (Figure 7) confirm the X-ray diffraction results. However, ECM leads to selective corrosion of the ferritic–pearlitic phase, which was already reported by Harst.\(^{[27]}\) Cementite acts nobler in comparison with ferrite. Therefore, selective dissolution of the less noble ferritic phase along the interphase ferrite/cementite was observed by SEM for ground and EDM 42CrMo4 after finishing by ECM. It is assumed that the observed dissolution of the austenitic phase occurs more uniformly. The penetration depth of the selective dissolution at the ground rim zone is lower compared with the EDM rim zone after surface finishing by ECM.

The topography of differently machined surfaces was characterized by means of the profile method. Table 9 shows the roughness parameters and reveals an increase in roughness parameters of the initial ground surface. In contrast, the roughness of initially EDM processed surfaces decreased significantly.

The experimental investigations revealed a less pronounced material removal by ECM for the rim zone obtained by grinding compared with the one obtained by EDM. Influencing factors were identified either to be the different nobility of the ferritic–pearlitic and austenitic phases, the specific roughness, or the overlaying oxygen evolution reaction at the specific surface at transpassive potentials. Simulation by commercial software (COMSOL Multiphysics) was performed to separate and evaluate those effects and to identify the relevant corrosion mechanisms.

Based on the simulations of ferritic–pearlitic 42CrMo4 at very high current densities of about 100 A cm\(^{-2}\), a simplified simulation model for ground ferritic–pearlitic 42CrMo4 at lower current densities of ~8 A cm\(^{-2}\) and smooth surface roughness of about \(R_{\text{max}} = 0.46 \mu m\) was developed. Figure 9a shows that the current density is homogenously distributed at the surface directly at the beginning of the ECM (\(t = 0\) s). However, locally the ferritic phase already starts to dissolve faster than the cementite phase. This leads to the
formation of small differences in height between the two phases, which is related to selective dissolution (Table 10). The height difference increases with increasing simulated processing time up to 10 s (Figure 9b) and finally reaches 0.26 μm.

In addition, an uneven current density distribution with higher current densities of 9.1 A cm$^{-2}$ at the protruding cementite lamella compared with 6.8 A cm$^{-2}$ at the ferritic phase was observed after 10 s. However, the corrosion rate of the cementite increases due to locally
increased current densities but is still smaller than for ferrite. It is known from the calculations\cite{27} that ferrite and cementite dissolve equally fast after reaching a cementite/ferrite current density ratio of 1.392. At this processing stage, a stationary height difference between these phases occur. Table 10 reveals that the system is close to approaching a stationary state already after 10 s.

Simulation of the EDM ferritic–pearlitic 42CrMo4 at current densities of ~8 A cm$^{-2}$ and high surface roughness of about $R_{\text{max}} = 11 \mu m$ reveal an inhomogeneous distribution of the current density at the starting point of the ECM process ($t = 0$ s; Figure 10a). The current densities are significantly higher (up to 14 A cm$^{-2}$) at the top of the resolidified austenitic deposits compared with the current densities of less than 1 A cm$^{-2}$ that were observed in the valleys of the formed craters. This inhomogeneous distribution of the current densities is reduced with increasing processing time up to 10 s by flattening the crater-like surface topography down to $R_{\text{max}} = 8.1 \mu m$ (Figure 10b).

### TABLE 10
Height differences and cementite/ferrite current density ratios obtained by simulation for ground 42CrMo4 surfaces

| $t$ (s) | Height difference between cementite and ferrite ($\mu m$) | Current density ratio between cementite and ferrite |
|--------|----------------------------------------------------------|-----------------------------------------------------|
| 0      | 0.00                                                     | 1.00                                                |
| 1      | 0.06                                                     | 1.07                                                |
| 2      | 0.10                                                     | 1.13                                                |
| 3      | 0.14                                                     | 1.18                                                |
| 4      | 0.17                                                     | 1.21                                                |
| 5      | 0.19                                                     | 1.24                                                |
| 6      | 0.21                                                     | 1.27                                                |
| 7      | 0.23                                                     | 1.29                                                |
| 8      | 0.24                                                     | 1.30                                                |
| 9      | 0.25                                                     | 1.32                                                |
| 10     | 0.26                                                     | 1.33                                                |

**4 | DISCUSSION**

The results on the influence of the rim zone modifications, obtained by grinding and EDM, on the electrochemical properties, revealed on the one hand, unstable passivation with a two-step passivation mechanism and on the other ternary passivation within the transpassive region for ground and EDM 42CrMo4. However, the ground rim zone modification revealed in general higher current densities as well as a more pronounced passivation mechanism within the passive region as well as in the transpassive region compared with EDM 42CrMo4.

Unstable passivation mechanisms typically depend on the cathodic process that predominates, such as hydrogen evolution, oxygen reduction, or metal cation reduction. Since sodium nitrate acts as a strong oxidizing agent, it is assumed that oxygen reduction predominates the corrosion mechanisms. Further, it is assumed that the unstable two-step passivation is related to the formation of more unstable and less protective passive layers for ground compared with EDM rim zone modifications of 42CrMo4. Fushimi et al.\cite{36} reported a higher carbon content of the oxide layer on the cementite phase compared with the ferritic phase. Therefore, it is assumed that a generally higher current density in the passive region can be related to the locally higher incorporation of carbon into the oxide layer for ground ferritic–pearlitic 42CrMo4 compared with EDM austenitic 42CrMo4. This leads to a higher defect density in the
oxide and thus to a reduced protective effect of the passive layer.

For ground 42CrMo4, a distinct secondary anodic current density maximum can be detected within the passive range. However, EDM 42CrMo4 exhibits only a weakly pronounced current density maximum. There are two general proposals for the formation of a current density maximum in steels. Firstly, France and Greene,[37] Hamm et al.,[38] and Ruel et al.[39] proposed, based on investigations on stainless steel in sulfuric acid, that the increase in current density is due to the dissolution of alloying elements such as chromium, nickel, and molybdenum. Schneider et al.[40] and Harst[27] concluded that the less pronounced secondary current density maximum. In addition, it is more relevant for this study. It was shown that all elements are transpassive at the secondary passivation potential of ground 42CrMo4. However, Ehle et al.[41] reported no significant compositional changes of chromium, molybdenum, and manganese within the rim zone for ground and EDM 42CrMo4. Therefore, the observed differences regarding the secondary anodic current density maximum between the two rim zone modifications cannot be fully related to the transpassive dissolution of the single elements.

The second hypothesis states that precipitated phases within the metallic matrix can also lead to the formation of a secondary anodic current density maximum. According to Rockel[41] it is likely that the single polarization curves of a metallic matrix and precipitated phases in chromium steel superimpose each other. Payer and Staehle[42] and Karner et al.[43] confirmed this observation for either TiC in AISI 321 steel or the sigma phase in AISI 316 steel and related this to the formation of a secondary current density maximum. In addition, Kadowaki et al.[44] observed a shift of the active range in anodic direction for the cementite compared with the ferritic phase for potentiodynamic measurements of the single ferritic or cementite phase in borate buffer solution at pH 8. A superimposition of the two polarization curves, as it can be assumed for ground 42CrMo4, would reveal a secondary anodic current density maximum. Harst[27] was able to confirm these results for pure cementite in sodium nitrate solution. According to these investigations, it is proposed that the cementite phase of ground ferritic–pearlitic 42CrMo4 steel is mainly responsible for the formation of the distinct secondary current density maximum. In addition, it is concluded that the less pronounced secondary current density maximum for EDM austenitic 42CrMo4 is related to the lack of cementite.

The transpassive potential range between 1.3 and 2 V_SCE includes a large number of overlapping processes, such as reactions of iron and chromium and the beginning of oxygen evolution.[14,45] Due to the differences between the passive layers on the ground ferritic–pearlitic compared with EDM austenitic 42CrMo4, different transpassive dissolution and transformation mechanisms of the passive layers were observed. In addition, significantly higher current densities in the transpassive area of ground 42CrMo4 indicates a change of the predominant reactions at the ground ferritic–pearlitic surfaces. ICP-MS measurements of the electrolyte after potentiostatic polarization at 2 V_SCE revealed that only 1% of the measured current density belongs to the dissolution of iron and chromium. Therefore, about 99% of the charge transfer is related to the oxygen evolution reaction. This observation was also confirmed by Lohrengel et al.[18] for iron in sodium nitrate. Since the current densities were normalized to the different roughness of the surfaces, the stronger oxygen evolution reaction of the ground surface at lower transpassive potentials of 2 V_SCE is attributed to different phases at the surfaces, such as ferritic–pearlitic versus austenitic phases, obtained by grinding and EDM. In addition, a proportionately higher dissolution of chromium compared with iron at lower transpassive potentials was observed. However, since Datta et al.[46] could not detect a ternary passive region in their investigations on pure iron in sodium nitrate solution, it is suggested that neither iron nor oxygen is responsible for the formation of this ternary passive region at 42CrMo4, but chromium.

A significant change of the corrosion mechanisms at higher transpassive potentials and high resulting current density combined with lower transpassive potentials were observed for ground and EDM 42CrMo4. This change is responsible for the efficiency of the material removal obtained by ECM. It was reported by Lohrenegel et al.[18] for iron in sodium nitrate that increasing current densities in the transpassive region result in a stronger dissolution of iron and a decrease of oxygen evolution. The ICP-MS measurements confirmed this observation also for ground and EDM 42CrMo4 after ECM finishing in sodium nitrate at high transpassive potentials and current densities. The transferred charge in the ECM, which was determined by measuring the current, was almost identical and calculated as 64–65 C for both surface conditions. Additionally, the measured current of 8 A cm⁻² at 15 V was constant over the processing time. Based on these results, the material removal was calculated by Faraday’s law, assuming ideal processing conditions. The same amount of material removal was obtained from these ideal calculations for both surface conditions (Table 3). However, the results of the ICP-MS measurements showed in the contradiction that ground 42CrMo4 dissolves electrochemically slower than EDM.
42CrMo4. Therefore, a change of the efficiency of ECM dependent on the rim zone modification is concluded.

Two main influencing factors for the different degrees of efficiency are proposed: First, the distance between the cathode and the 42CrMo4 surface and second, the chemical and microstructural modifications of the rim zones. The distance between the cathode and 42CrMo4 surfaces is strongly related to the surface roughness. A smooth surface, for example, obtained for the ground 42CrMo4, results in a more homogenous current density distribution with a constant cathode to anode distance. Whereas rough EDM surfaces should show heterogeneous current density distributions with higher current densities at the highest peak and lower current densities in the lower valleys. This leads to shorter and greater distances between the cathode and the anode as well as to locally inhomogeneous material removal. Münninghoff, [20] Rosenkranz, [19] and Haisch et al. [34] reported for iron in sodium nitrate that locally increased current densities lead to an accelerated dissolution of the transpassive dissolution. Based on these results as well as the topographical analysis by SEM and confocal microscopy before and after ECM (Figures 3, 4, 7, and 8) and the observed decreased material removal by ICP-MS for ground compared with EDM 42CrMo4, it is assumed that the surface roughness directly influences the process efficiency of the different rim zone modifications with time.

Focusing on the change of the roughness of the austenitic EDM surface rim zone modification, it was observed that the roughness is reduced by about 32% after 10 s ECM processing time. This is supported by additional FEM simulations (Figures 9 and 10) at the beginning and after 10 s of ECM, dependent on the roughness. In addition, Sautebin et al. [22] reported on FEM simulations on the influence of roughness on the surface, finishing by ECM and demonstrated a smoothing effect of rough surfaces. However, the results of the own FEM simulation showed an average material removal, which is about twice the material removal measured by ICP-MS. One relevant parameter of the FEM simulation that might lead to this error, is given by the proportionality constant K. This constant describes the relationship between the efficiency and the current density. Within the calculations, an overall efficiency of 19% was used for EDM 42CrMo4 after ECM for 10 s. Although this parameter was adjusted to the experimental data, it has to be considered that the efficiency is locally different at the surfaces and process time-dependent. Therefore, further development of the used simulation is necessary and the focus of future work.

It is assumed that in addition to the influence of surface roughness, there is also an influence of the microstructure of the two rim zone modifications. The experimental and simulation results of ground 42CrMo4 revealed that at the beginning of the ECM process (t = 0 s) a uniform current density distribution occurs, which changes with increasing processing time toward an inhomogeneous current density distribution due to selective corrosion of the ferritic phase. These results are confirmed by investigations of Klocke et al. [24] It was reported that the ferritic phase preferentially dissolves electrochemically, while cementite lamella remain intact during ECM processing of ferritic–pearlitic 42CrMo4. However, Borchers et al. [10] did not observe a preferred dissolution of ferrite in ECM processed ferritic–pearlitic 42CrMo4. Hars [27] related these different results to the formation of different electric fields. At low electric field strengths, a strongly pronounced selective dissolution of the ferritic phase was postulated, whereas at high electric field strengths, an equal dissolution rate of ferrite and cementite was suggested. For ground 42CrMo4, after 10 s ECM at 15 V in sodium nitrate solution, an increased amount of cementite can be detected on the surface due to the selective dissolution of the ferrite compared with the cementite lamellae. The ECM processing therefore has an influence on the phase distribution at the surface of ground 42CrMo4 with increasing processing time.

Furthermore, it is suggested that the amount of the cementite phase also has an impact on the efficiency of surface finishing by ECM considering the experimental and the simulation results of ground 42CrMo4. This suggestion is supported by the efficiency studies of the ECM process of cementite and iron in sodium nitrate solution of Münninghoff. [20] Significantly lower efficiency of cementite compared with iron was observed. This observation is associated with an increased oxygen evolution within the transpassive region at high potentials considering charge neutrality. Therefore, the slower material dissolution of ground ferritic–pearlitic 42CrMo4 compared with the higher material dissolution for EDM austenitic 42CrMo4 after ECM is associated with the slower dissociation of the cementite phase. Summarizing, both rim zone modifications, the surface roughness as well as the microstructure, revealed a strong impact on the amount of the material removal by ECM of ground and EDM 42CrMo4. The lower roughness as well as the higher oxygen evolution related to cementite explains the lower efficiency and amount of material removal by ECM for the surface finishing of ground compared with EDM 42CrMo4.

5 CONCLUSIONS

In this study, the influence of rim zone modifications obtained by grinding and EDM on the efficiency of material removal during ECM surface finishing was investigated. The different rim zones were analyzed with
respect to their topography, the present phases, and their electrochemical properties in the electrolyte used during ECM. By linking these rim zone modifications with the measured material removal in ECM, influencing variables on the efficiency of ECM could be identified by experiment and FEM simulation. The following conclusions are drawn:

- A strong influence of the rim zone modifications, obtained by grinding and EDM, on the electrochemical properties, were observed. An unstable passivation with a two-step passivation mechanism and a ternary passivation within the transpassive region for ground and EDM 42CrMo4 were identified.
- The ground rim zone modification revealed in general higher current densities as well as a more pronounced passivation mechanism within the passive as well as the transpassive region compared with EDM 42CrMo4. It is assumed that more oxygen evolves on ground surfaces compared with EDM surfaces at the same, low transpassive potential.
- The material removal of ground 42CrMo4 during ECM surface finishing at very high transpassive potentials is smaller than for EDM 42CrMo4 at the same transferred charge, which indicates a lower efficiency of material removal.
- It is concluded that both rim zone modifications with different roughness and a ferritic–pearlitic or austenitic microstructure influence the efficiency of ECM.
- A locally increased current density due to heterogeneous distance distribution between anode and cathode leads to improved efficiency of ECM for rough EDM premachined surfaces and therefore to a higher total material removal compared with ground 42CrMo4.
- In addition, the cementite phase has a negative influence on the efficiency of ECM of ferritic-pearlitic ground 42CrMo4 due to locally higher oxygen evolution. This explains the increased material removal of EDM 42CrMo4 with predominantly austenitic microstructure.

ACKNOWLEDGMENTS

The authors would like to thank Martina Thoennissen, Elke-Scharberger-Zimmermann (both RWTH Aachen University, Foundry Institute), Simon Evertz (RWTH Aachen University, Materials Chemistry), Dr. Daniel Röhrens as well as Roland Salber (both Access GmbH) for technical support and their contribution to experimental work. In addition, the authors would like to thank Sebastian Schneider (RWTH University, WZL) for providing the 42CrMo4 EDM samples. This project is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)-Projektnummer 223500200-TRR 136, subproject M06.

CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

AUTHOR CONTRIBUTIONS

Daniela Zander: conceptualization, methodology, roles/writing—original draft, writing—review and editing, supervision, funding acquisition, resources, and project administration. Alexander Schupp: investigation, data curation, formal analysis, visualization, roles/writing—original draft, writing—review and editing, and project administration. Stefanie Mergenthaler: investigation, data curation, roles/writing—original draft. René D. Pütz: investigation, data curation, roles/writing—original draft, writing—review and editing, supervision, and project administration.

DATA AVAILABILITY STATEMENT

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

ORCID

Daniela Zander http://orcid.org/0000-0001-9420-1847
René D. Pütz http://orcid.org/0000-0002-6627-6443

REFERENCES

[1] S. Hizume, W. Natsu, Procedia CIRP 2018, 68, 746.
[2] C. D. Zhou, E. J. Taylor, J. J. Sun, L. Gebhart, E. C. Stortz, R. P. Renz, Trans. NAMRI/SME 1997, 25, 147.
[3] A. Lozano-Morales, L. Gebhart, M. Inman, E. J. Taylor, P. O. Miller, J. Appl. Surf. Finishing 2007, 2, 192.
[4] S. C. Tam, N. H. Loh, S. Miyazawa, Int. J. Prod. Res. 1989, 27, 1757.
[5] K. P. Rajurkar, M. M. Sundaram, A. P. Malshe, Procedia CIRP 2013, 6, 13.
[6] T. Gretzki, C. Krause, I. Frolov, T. Hassel, M. Nicolaus, F. W. Bach, M. Kästner, O. Abo-Namous, E. Reithmeier, Steel Res. Int. 2009, 80, 906.
[7] H. Koehler, K. Partes, T. Seefeld, F. Vollertsen, Phys. Procedia 2011, 12, 512.
[8] D. Zander, A. Klink, S. Harst, F. Klocke, C. Altenbach, Mater. Corros. 2019, 70, 2190.
[9] L. C. Ehle, S. Schneider, A. Schwedt, S. Richter, A. Klink, J. Mayer, J. Mater. Process. Technol. 2020, 280, 116596.
[10] F. Borchers, B. Clausen, S. Eckert, L. Ehle, J. Epp, S. Harst, M. Hettig, A. Klink, E. Kohls, H. Meyer, Metals 2020, 10, 895.
[11] K. W. Mao, J. Electrochem. Soc. 1971, 118, 1870.
[12] K. W. Mao, J. Electrochem. Soc. 1971, 118, 1876.
[13] J. P. Hoare, K. W. Mao, J. Electrochem. Soc. 1973, 120, 1452.
[14] D. T. Chin, K. W. Mao, J. Appl. Electrochem. 1974, 4, 155.
[15] F. Klocke, S. Harst, M. Zeis, A. Klink, Procedia CIRP 2016, 42, 396.
[16] S. Mehrafsun, S. Harst, O. Hauser, S. Eckert, A. Klink, F. Klocke, F. Vollertsen, Procedia CIRP 2016, 45, 347.
[17] M. M. Lohrengel, C. Rosenkranz, Corros. Sci. 2005, 47, 785.
[18] M. M. Lohrengel, C. Rosenkranz, D. Rohrbeck, Microchim. Acta 2006, 156, 163.
[19] C. Rosenkranz, Ph.D. Thesis, Heinrich-Heine-Universität Düsseldorf, Germany, 2005.
[20] T. R. Münninghoff, Ph.D. Thesis, Heinrich-Heine-Universität Düsseldorf, Germany, 2012.
[21] M. M. Lohrengel, I. Klüppel, C. Rosenkranz, H. Bettermann, J. W. Schultze, Electrochim. Acta 2003, 48, 3203.
[22] R. Sautebin, H. Froidevaux, D. Landolt, J. Electrochem. Soc. 1980, 127, 1096.
[23] T. Gurumurthy, O. V. Krishnaiah Chetty, V. Radhakrishnan, Int. J. Prod. Res. 1978, 16, 453.
[24] F. Klocke, S. Harst, F. Karges, M. Zeis, A. Klink, Procedia CIRP 2017, 58, 169.
[25] F. Klocke, S. Harst, M. Zeis, A. Klink, Procedia CIRP 2018, 68, 505.
[26] A. Klink, Procedia CIRP 2016, 42, 240.
[27] S. Harst, Ph.D. Thesis, RWTH Aachen, Germany, 2019.
[28] T. Bergs, S. Harst, CIRP Ann. 2020, 69, 153.
[29] DIN EN ISO 16610-21, Geometrical product specifications (GPS), 2013.
[30] DIN EN ISO 16610-31, Geometrical product specifications (GPS), 2017.
[31] DIN EN ISO 25178-2, Geometrical product specifications (GPS), 2012.
[32] DIN EN ISO 17475, Corrosion of metals and alloys, 2008.
[33] ASTM G 5, Standard Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements, 2014.
[34] T. Haisch, E. Mittemeijer, J. W. Schultze, Electrochim. Acta 2001, 47, 235.

[35] Deutsche Edelstahlwerke, Material Data Sheet 42CrMo4, https://www.dew-stahl.com/fileadmin/files/dew-stahl.com/documents/Publikationen/Werkstoffdatenblaetter/Baustahl/1.7225_1.7227_de.pdf (accessed: November 2020).
[36] K. Fushimi, R. Nakagawa, Y. Kitagawa, Y. Hasegawa, J. Electrochem. Soc. 2019, 166, C3409.
[37] W. D. France Jr, N. D. Greene, Corrosion 1968, 24, 403.
[38] D. Hamm, K. Ogle, C. O. Olsson, S. Weber, D. Landolt, Corros. Sci. 2002, 44, 1443.
[39] F. Ruel, P. Volovitch, L. Peguet, A. Gaugain, K. Ogle, Corrosion 2013, 69, 536.
[40] M. Schneider, L. Simunkova, M. Manko, M. M. Lohrengel, W. Hoogsteen, J. Solid State Electr. 2019, 23, 345.
[41] M. B. Rockel, Corrosion 1971, 27, 95.
[42] J. H. Fayer, R. W. Staehle, Corrosion 1975, 31, 30.
[43] W. M. Karner, M. Y. Nazmy, A. Arfaj, Mater. Corros. 1980, 31, 446.
[44] M. Kadowaki, I. Muto, K. Takahashi, T. Doi, H. Masuda, H. Katayama, K. Kawano, Y. Sugawara, N. Harai, J. Electrochem. Soc. 2019, 166, C345.
[45] E. Rosset, M. Datta, D. Landolt, J. Appl. Electrochem. 1990, 69, 69.
[46] M. Datta, H. J. Mathieu, D. Landolt, J. Electrochem. Soc. 1984, 131, 2484.

How to cite this article: Zander D, Schupp A, Mergenthaler S, Pütz RD, Altenbach C. Impact of rim zone modifications on the surface finishing of ferritic-pearlitic 42CrMo4 using electrochemical machining. Materials and Corrosion. 2020;1–15. https://doi.org/10.1002/maco.202012213