Interdiffusion Coatings for High-Temperature-Corrosion Protection of Low-Alloy Steels

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Abstract: In this study, the creation of an oxidation-protection layer system composed of Fe and Cr on top of a plain or ultra-low carbon steel substrate by means of electroplating was investigated. By applying an appropriate heat treatment, interdiffusion takes place transforming the individual layers into a gradient structure with stainless-steel-like properties. The experimental work includes interdiffusion experiments on single-layer systems, i.e., Cr deposition on plain or ultra-low carbon steel. Earlier work shows a strong influence of carbon on the interdiffusion behavior in Cr-layer systems. Therefore, an experimental setup of Cr-layer systems with different thicknesses is realized and discussed where carbon steel was used. A. The analysis of the resulting interdiffusion layers was carried out by means of scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectroscopy (EDX). Furthermore, the specimens were oxidized in laboratory air at 700°C for various time periods. The respective oxidation behavior of the manufactured systems was characterized by applying analytical SEM to ground and polished cross sections. For interpretation of the results, a new modeling approach, where the relevant interdiffusion processes are simulated by means of the cellular automata approach, was applied to the systems mentioned above to optimize the interdiffusion layers for high-temperature oxidation protection.

Keywords: interdiffusion layers, stainless steel coatings; cellular automata, oxidation resistance
Introduction

The problem of hot corrosion and high temperature oxidation narrows the application range of engineering alloys for many industrial utilizations. In applications like radiant tube or heat exchanger components inside a power plant, the service life of the used alloys is defined by their long-term oxidation behaviour and creep resistance [1-3]. Superheater tubes are designed for operating temperatures between 400°C and 700°C, where their surface is exposed to combustion atmospheres at the outer side, while the inner side must withstand the contact with water vapor atmospheres. In case of solar-thermic power plants, the tubes are exposed to salt melts and a deeper understanding of their corrosion is described in [4,5]. The contact with combusting atmospheres on the outer side can lead to a degradation and an external scale at the unprotected surface of an alloy. An example can be seen in Figure 1. Depending on the chemical composition of the atmosphere, various internal corrosion products may be formed, like internal oxides, nitrides [6-8], carbides or sulphides [9]. In addition, metal dusting may occur [6,10,11]. The resulting time-dependent loss of wall-thickness limits the lifetime of the corrosively stressed parts. Due to their acceptable corrosion resistance and cost-performance ratio, low-Cr steels are mostly used in power generation. The desired improvements of efficiency require an increase in the operating temperature of power plants, and therefore, the application of high Cr austenitic stainless steels or even more expensive Ni-based alloys becomes necessary [1,2].

Figure 1. (a) Low carbon steel RS275 after exposure to laboratory air for 100 h at 700 °C with an electroplated Cr-interdiffusion layer on top and left / bottom side unprotected. (b) ultra-low carbon steel after similar exposure, the Cr-interdiffusion layer is covering the top and the bottom, while the left side is unprotected. (both pictures taken from own work).

Diffusion coatings as an alternative to expensive alloys may be used to protect plain carbon steels from internal and external corrosion that is shown in Figure 1 for two different types of substrate materials that are investigated in this study. The formation of protective layer systems, resulting from an enhanced solute concentration at the surface of the samples, where reported for a Cr$_2$O$_3$ layer formation in steels[12,13], and in Ni-based alloys with the formation of Al$_2$O$_3$ [14] using protective coatings and surface treatments. Regarding diffusion coatings, elements that are applied on a substrate material diffuse into the substrate, leading to a change of the chemical composition near the surface towards a corrosion-resistant coating. Well-known methods used in the industrial area are the pack cementation and chemical vapour deposition [15]. Diffusion coatings and their exposure to corrosive environments were subject of the research of Schmidt et al. [16,17], where ferritic-martensitic steel in water vapour atmosphere was investigated. The works of Naji et al. [18,19] and Jha et al. [20,21] focused on the Al diffusion and Pt-modified aluminide diffusion coatings on Ni-base superalloys, cf. [22-24].
The main topic of this study is the application of a Cr diffusion layer on the surface of plain carbon steels. The method of choice for Cr deposition is electroplating, which is already recognized as a decent production technique for coatings on objects of complex geometry [25]. Followed by diffusion annealing, interdiffusion between the substrate and the Cr layer takes place, creating a gradient corrosion-resistant layer of high adherence, which is therefore called "synthetic stainless-steel-like diffusion layer". By solving the diffusion differential equation by numerical methods, like the finite difference method (FDM), the cellular automata approach, in combination with the computer-based calculation of phase diagrams (CALPHAD), interdiffusion process can be calculated in advance and thus, the coating structure can be designed even beforehand the industrial production has started. However, the underlying mathematical model has to consider the concentration-dependent effective interdiffusion coefficient \( \tilde{D} \), which is itself dependent on the diffusivities of each diffusing element [26]. Furthermore, the Kirkendall effect plays a significant role during the interdiffusion process and has to be taken into account [27]. These aspects are necessary to explain the formation of voids or the deformation of material occurring during the diffusion process [28] as well as the generation of internal stresses [29,30].

**Experimental details**

On a substrate, either a commercial plain carbon BS EN 10025-2 of type RS275 [31] or an ultra-low carbon steel (ULCS) (chemical compositions see Table 1) Cr coatings were applied by electroplating. While the electroplating of the RS275 substrate (CR/RS275) took place at Surface Engineering and Nanotechnology Institute at Cranfield University/UK, the samples with ultra-low carbon steel (Cr/ULCS) as a substrate, were produced by a Rudolf Jatzke – Günther Holthöfer GmbH & Co. KG. The bath specifications are summarized in Table 2.

### Table 1. Chemical composition of RS275 in wt. % [24].

<table>
<thead>
<tr>
<th>Designation</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS275</td>
<td>0.18-0.22</td>
<td>1.50</td>
<td>0.025-0.035</td>
<td>0.025-0.035</td>
<td>0-0.012</td>
<td>0.55</td>
<td>balance</td>
</tr>
<tr>
<td>ULCS</td>
<td>&lt; 0.001</td>
<td>0.042</td>
<td>0.004</td>
<td>0.018</td>
<td>0.022</td>
<td>0.018</td>
<td>balance</td>
</tr>
</tbody>
</table>

### Table 2. Bath compositions for electroplating.

<table>
<thead>
<tr>
<th>Chromic acid bath</th>
<th>Composition</th>
<th>Temp. / °C</th>
<th>Current density / A/dm²</th>
<th>Voltage / V</th>
<th>Time / min.</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>on RS275</td>
<td>CrO₃ (250 g/L)</td>
<td>40-50</td>
<td>50</td>
<td>4.5-5.0</td>
<td>57</td>
<td>Ti mesh + Cr pellet</td>
</tr>
<tr>
<td></td>
<td>H₂SO₄ (2.5 g/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n/a</td>
</tr>
<tr>
<td>on ULCS</td>
<td>CrO₃ (250-280 g/L)</td>
<td>56-58</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>H₂SO₄ 3% of the solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n/a</td>
</tr>
</tbody>
</table>

All specimens were vacuum annealed at 1030°C for a duration of 24 h, resulting in the formation of a stainless-steel-like interdiffusion layer protecting the sample from oxidation. The samples were exposed to laboratory air at 700°C for 100 h for investigation of the oxidation behaviour. All specimens were cut, ground and polished in order to create cross-sections of the vacuum-annealed and oxidized samples. Microstructural characterization was carried out by means of scanning electron microscopy (SEM Zeiss Auriga FEG) in combination with energy-dispersive X-ray spectroscopy (EDX). For the EDX measurements, an Oxford silicon drift detector (X-Max 80 mm²) was used.
Results and discussion

Interdiffusion behaviour

The layer systems presented in this study are Cr layers on top of RS275 and ULCS steel, respectively. Figure 2 shows BSE images and EDX analyses of both systems after electroplating. The thickness of the Cr layer in Figure 2a (Cr/RS275) is about 88 µm, and a well-defined interface between the Cr layer and the substrate can be observed (c.f. Figure 2c). Figure 2b shows the Cr/ULCS system after electroplating. The layer thickness in this system is around 48 µm and, as in Cr/RS275, a well-defined interface between the Cr layer and the substrate is present.

![Figure 2](image)

**Figure 2.** Metallographic cross sections of Cr/RS275 (a) and Cr/ULCS (b) analyzed by back-scattered electron imaging (BSE) and EDX-line scan of each system (c) and (d), after electroplating.

After annealing in vacuum for 24 hours at 1030°C, both systems show an interdiffusion zone which can be seen in the SEM micrographs in Figure 3a and 3b and the resembling concentration profiles of Figure 3c and 3d, respectively. It becomes obvious that the interdiffusion zone of the Cr/ULCS system is wider (133 µm) than the one of Cr/RS275 (105 µm). In both systems, no indications of any corrosion were found. The diffusion of Fe in Cr/ULCS reached the surface of the Cr layer and a ratio of 60 at. % of Cr and 40 at. % of Fe is established. As described in [32], the Cr/RS275 system has an original Cr layer of 10 µm width after annealing. There, it was shown qualitatively that an accumulation of C coming from the low carbon steel substrate is occurring. A similar effect was observed and further explanation is given in [33,34], where forming of Cr$_2$3C$_6$ carbide phase is presumed. Such accumulation effect as observed in Cr/RS275 are not occurring in the Cr/ULCS system, due to the significantly lower amount of C in the substrate material. For the interdiffusion process, the
amount of carbon in the substrate plays a significant role. Due to the carbon accumulation in the Cr/RS275 system, where a Cr-C enriched zone is established, the diffusion of Cr into Fe and vice versa is at least slowed down (cf. Figure 3c). While the concentration profiles in Cr/ULCS where no C accumulation was observed show the expected monotonically decreasing slope (cf. Figure 3d), there is a significant drop in the concentration profiles at the Cr-Fe interface in the Cr/RS275 system. Kirkendall voids underneath the Cr layer in the Cr/RS275 and near the surface of the sample in the Cr/ULCS system can be observed [27].

![Metallographic cross sections of Cr/RS275 (a) and Cr/ULCS (b) analyzed by back-scattered electron imaging (BSE) and the respective EDX-line scans (c) and (d), after 24 h heat treatment in vacuum at 1030°C.](image)

**Figure 3.** Metallographic cross sections of Cr/RS275 (a) and Cr/ULCS (b) analyzed by back-scattered electron imaging (BSE) and the respective EDX-line scans (c) and (d), after 24 h heat treatment in vacuum at 1030°C.

**Oxidation behavior**
In Figures 4a to 4d, the results after exposure to laboratory air for a duration of 100 h and 30 h at 700°C are represented. After a 100 h exposure, see Figure 4a, the remaining chromium oxide scale in the Cr/RS275 is spalled (cf. Figure 3a). At the surface of the remaining sample, a chromium-carbide-rich scale is formed due to the interdiffusion process as discussed earlier. Underneath the scale, Fe oxidizes, and mainly wustite is formed inside the Kirkendall voids, according to the EDX analysis. Furthermore, the exposure to air leads to precipitation of chromium carbides inside the interdiffusion zone, which is depicted in Figure 4a. A possible explanation is given in [32]: During exposure to air at 700 °C, the chromium carbide surface layer oxidizes and releases carbon, whichdiffuses into the interdiffusion zone leading to internal carburization. Furthermore, this effect has its origin at the surface of the sample which becomes obvious after comparing the results from 30 h exposure to air (see Figure 3c), where no formation of chromium carbides was observed. If the chromium carbides would originate from the C content of the substrate, a chromium carbide formation would directly occur at the substrate-side of the interdiffusion zone, which is not the case in the investigated sample.
In Figure 4b and 4d, the BSE micrographs of the cross sections of the Cr/ULCS system after 100 h and 30 h exposure to laboratory air are shown, respectively. Due to the formation of a protective Cr oxide scale, there are no signs of corrosion. A distinct difference between the Cr/ULCS and the Cr/RS275 system is the lack of chromium carbide formation that is visible in Figure 4a and 4c. The missing of any chromium carbides is based on the fact that no C reservoir is formed during vacuum annealing (see Figure 3). Thus, no released carbon may diffuse into the interdiffusion zone from the surface and internal carburization is prevented. These results emphasize the hypothesis stated in [32] that a C reservoir is indeed formed during vacuum annealing when a sufficient high amount of C is present in the substrate material. Compared to Cr/RS275 system, the Kirkendall voids near the surface stay empty during the whole exposure time and no wustite is build inside as it is the case for the Cr/RS275 system. Here, the interdiffusion zone established during the annealing process acts as chromium reservoir, and despite the internal carburization in the Cr/RS275 system, both systems are able to effectively protect the substrate from the corrosion.

![Figure 4](image)

**Figure 4.** Metallographic cross sections of Cr/RS275 (a) and Cr/ULCS (b) analyzed by back-scattered electron imaging (BSE) after exposure to laboratory air for 100 h at 700°C after vacuum heat treatment at 1030°C for 24 h. Metallographic cross sections of Cr/RS275 (c) and Cr/UCLS (d) analyzed by back-scattered electron imaging (BSE) after exposure to laboratory air for 30 h at 700°C after vacuum heat treatment at 1030°C for 24 h.

The importance of the interdiffusion process for the corrosion behaviour is shown in Figure 5. The observed Cr/ULCS system exhibits a much thinner Cr layer after electrodeposition (about 30 µm). All other treatments in terms of annealing and exposure are equal as presented above. The difference to 18 µm Cr layer thickness leads to different concentrations of Cr (27 at.%) and Fe (73 at.%) at the surface of the sample. Exposed to air, it becomes clear that although a Cr oxide layer is build, the interdiffusion layer is only able to slow the corrosion process. As it can be seen in Figure 5, Fe oxide is built at the surface and inside the Kirkendall voids.

At this point, it is important to mention both, (i) that the operating time of targeted power plant components is by order of magnitudes higher and (ii) that the ultra-low carbon steel used here
is of poor mechanical properties when it comes to high temperature applications. However, the relatively simple system discussed here is a reasonable concept for fundamental understanding of the interdiffusion systems and their behaviour with regard to corrosion and diffusion process. The presented interdiffusion coatings are possibly effective in terms of protecting the substrate compared to the corrosion attack seen in Figure 1.

![Figure 5. Metallographic cross sections of Cr/ULCS with originally 28 µm Cr layer analyzed by back-scattered electron imaging (BSE) after exposure to laboratory air for 100 h at 700°C after vacuum heat treatment at 1030°C for 24 h.](image)

**Modelling concept**
In order to predict the gradient structure of interdiffusion coatings, the presented study is meant to be the experimental basis for the adaptation of the cellular automata simulation. The cellular automata approach was successfully applied to simulate diffusion-controlled precipitation processes [35-37] and intergranular oxidation [37,38]. A first model for the description of interdiffusion processes was discussed in [39]. The two-dimensional simulated diffusion area is discretized into a distinct number of cells, whereby the cells are assigned either by the state particle A, particle B or vacancy. The diffusion movement of the particles is realized by the concept of Chopard and Droz [40]. The diffusing particles take one of four directions for movement considered in the next iteration step: they may be deflected by 90° with a probability \( p_1 \), reflected by 180° with a probability \( p_2 \) or follow its former direction with a probability \( p_0 \). According to Chopard and Droz, the diffusion coefficient \( D \) of each diffusing species may be expressed by these probabilities [40]. Depending on the respective probability, the species will proceed into one of the surround cells in the next iteration step, but only if this distinct cell is in state “vacancy” and thus occupied by particle A or B. In the case of two neighbouring cells, both occupied by different kind of particles, the particles may switch positions with a probability \( p_s \).
Figure 6. Interdiffusion of Cr and Fe at 1030°C as simulated by the cellular automata approach, (a) diffusion profile (white: Cr, blue: Fe), and (b) resembling concentration profile.

An example for a calculated concentration profile for interdiffusion of Cr (diffusion coefficients: 

\[ D_{\text{Cr in } \alpha-\text{Fe}} = 7.65 \times 10^{-10} \text{ cm}^2/\text{s}, \quad D_{\text{Cr in } \gamma-\text{Fe}} = 2.20 \times 10^{-11} \text{ cm}^2/\text{s} \]  

[41,42]) and Fe (diffusion coefficient: 

\[ D_{\text{Fe in Cr}} = 3.6 \times 10^{-11} \text{ cm}^2/\text{s} \]  

[43]) (24 h at 1030 °C) is shown in Figure 6. During the diffusion of Cr into Fe a phase transition around 15 at.% takes place. The simulation considers this transition by adjusting the transition probabilities for Cr as soon as an amount of 15 at.% Cr in Fe is reached. Although the concentration profiles from Figure 3c and 3d are not exactly reproduced, the example in Figure 6 demonstrates that it is possible to simulate an interdiffusion process with two different species of different diffusivities.

Conclusions
In the study, it was shown that it is generally possible to create an oxidation-resistant layer system consisting of Cr on a low-carbon and ultra-low carbon steel by electroplating. On top of a low carbon steel with a Cr layer system, an accumulation of C was observed after vacuum annealing, which is not taking place in the Cr/ULCS system due to the significantly lower amount of C in the substrate. By means of oxidation tests at 700°C, it was demonstrated that the layer systems are generally capable to protect both substrates (low-carbon steel and ultra-low-carbon steel) from oxidation. This becomes obvious when comparing the results of the oxidation experiments for the protected and unprotected sides of the sample, where a massive degradation of the substrate takes place on the non-protected sides without interdiffusion layer. The difference between both systems is that in case of the Cr/RS275 system, the formation of chromium carbides is occurring, which is missing in the Cr/ULCS system. Again, the reason is the low amount of C in the ULCS substrate. In addition, it was shown that the thickness of the applied layers prior to vacuum interdiffusion heat treatment is crucial for the corrosion resistance properties. Further investigation on the long-term behavior have to be performed after an adaption of the sample geometry due to the obvious corrosion from the unprotected side.

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References
27. E. Kirkendall, L. Thomassen, C. Upthegrove, Transactions of the AIME, 133 (1939) 186.