The Effects of Cr/Mo Micro-Alloying on the Corrosion Behavior of Carbon Steel in CO2-Saturated (Sweet) Brine under Hydrodynamic Control

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The development of high durability and low cost materials able to operate in a broad range of increasingly aggressive exposure conditions is critical for the oil and gas industries. Of the practical exposure conditions in the oil-field and pipelines, acidic pH (comprising aqueous CO2 and/or H2S) and region-specific elevated temperatures are common. In these environments sulfide or carbonate based scales are typically formed on the surface of the steel. These scales can have varying degrees of protective properties. The steel can potentially be made more durable therefore, by enhancing the formation of a protective, adherent, non-porous crystalline scale on the surface of the corroding steel. This type of protective scale could in principle be encouraged to form by controlling the most important exposure conditions such as pH and temperature; however as temperature is more or less fixed for a particular location, it is difficult to find any practically feasible technique of controlling the exposure temperature. However, if one could control local solution conditions at the surface of the steel, such that the interfacial conditions favor the precipitation of a protective crystalline scale, then inherent corrosion resistance is provided to the material. One of the most interesting techniques that can be considered for modifying the local environment is micro-alloying: i.e. incorporating a small amount of a specific element into a base material for the purpose of achieving the desired properties.

Amongst the various alloying elements, Cr micro-alloying (<2 wt%) has been found to be effective in improving the durability of oil-field grade plain carbon steels in CO2 environments.1-7 A number of studies8-12 have also used low alloy steels with Mo concentrations of around 0.2 ± 0.05 wt% often used in combination with Cr in the range of 0.5–3 wt%. All show a significant improvement in corrosion performance, including a significant reduction of pitting corrosion, associated with the formation of a less porous and better adherent and protective scale compared to the non-alloyed steel. There appear to be several different aspects to the mechanism for the protective effect of Cr, dependent upon the solution pH and steel microstructure. Our earlier work12,13 with solutions saturated in CO2 at atmospheric pressure, at 80 °C and pH 6.8, indicated as the important effects a decrease in the critical supersaturation, and enhancement of the crystallization rate of siderite in the presence of Cr14. Studies at higher CO2 pressure, with temperature 80 °C and pH < 5.6, on a range of alloys having from 1 to 6.5 wt% Cr,15-19 have shown the formation of an amorphous layer on the order of 20 μm thick of a mixed Cr(OH)2-FeCO3 as the critical phenomenon for decreasing the corrosion rate, the open-circuit corrosion rate falling sharply for Cr content >2%.19 Crystalline siderite could form on top of this amorphous layer, and pH was found to be critical, presumably because it altered the dissolution rate of both the crystalline siderite and of the amorphous FeCO3. As expected, flow was shown to be important through its effect on supersaturation and precipitation of both FeCO3 and Cr(OH)3.19 The distribution of Cr between different elements of the microstructure also appeared to be important, perhaps because that affected the dissolution rate of Cr from the alloy. Alloying and heat-treatment also changed the amount and morphology of Fe2C, which can act as the cathodic site in open-circuit corrosion;15 corrosion of different microstructures further changes the interfacial roughness, which changes the local supersaturation and hence scale precipitation kinetics.16 Amorphous Cr(OH)3 was found to precipitate preferentially in areas where corrosion pits were forming, and inhibited their propagation.18

The effect of Mo however has not been well-addressed in the literature and the individual effect of Mo on the scale formation and its protective nature is unclear. The effect of Cr alone has been assumed to be responsible for the improved corrosion performance of the alloys studied in the literature, and the potential effects of low levels of Mo in the steels have not been discussed. Kermani et al.10 tested a range of steels containing 1.5–3 wt% Cr and 0.3 wt% Mo, and indicated that the presence of Mo was beneficial in reducing the critical corrosion current for the onset of a protective film. They suggested that in an acidic pH range (pH ~5), a minimum level of Cr of around 3 wt% is required for an acceptable corrosion resistance (~0.05 mm/yr). They further suggested a beneficial effect of Mo in the presence of optimized Cr (2-3 wt%). However, they did not put forth any mechanistic interpretation of the effect of either Mo, or Mo in the presence of Cr. Edmond and Cochrane11 performed flow-loop tests for a series of low alloy steel samples where Cr varied from 0 to 5 wt% and Mo varied from 0 to 0.5 wt%. They showed that the addition of Cr up to 5 wt% was very effective in reducing the corrosion rate and that the addition of Mo was beneficial to the corrosion protection. However,
mechanistic determinants of the Cr and/or Mo effect on the corrosion protection behavior were not explored. Al-Hassan et al. used a steel (UNS-J22090) containing as high as 1.37 wt% of Mo in combination with 2.3 wt% of Cr. They presumed that the alloying elements reduced active dissolution and hence the overall corrosion rate by increasing the corrosion resistance of the ferritic metal phase and/or preventing the formation of cementite (Fe₃C). However, the authors did not attribute the superior scale protectiveness to the presence of Mo.

The majority of the work that has dealt with steels containing both Cr and Mo as minor alloying elements has only generally attempted to explain the overall improvement in terms of reduction of corrosion rate and scale protectiveness, without showing any decoupled effect of Mo or its potential synergistic interaction with Cr. Therefore, whether a combination of Cr with other alloying elements, such as Mo, can yield a superior behavior needs deeper investigation along with careful interpretation of the mechanistic effects.

The bulk of the work found in the literature on the effect of microalloying is under static to quasi-static condition. The little information available in the literature under high flow conditions is often contradictory, mainly because of the different exposure conditions in terms of temperature and/or pH. Our previous work demonstrated that, at pH >6.5 and at 80°C, anodic dissolution of plain carbon steel to form a colloidal product proceeded in parallel with an anodic electrocrystallization reaction that resulted in a crystalline scale. The dissolution current and the surface supersaturation were shown to be controlled by the thickness of an initially-formed amorphous layer, the supersaturation being determined by the precipitation rate constant of colloidal FeCO₃ and by the product of the current for Fe dissolution and the diffusion boundary layer thickness. Traces of Cr⁺⁺ in the solution significantly accelerated the precipitation rate of the colloidal precursor and accelerated the appearance of the crystalline scale. Traces of molybdate in the solution also affected the rate of formation of crystalline spherulite.

In the present study, we extend our previous work to investigate the effects of Cr/Mo micro-alloying (with ~1–3.5 wt% Cr and 0–0.7 wt% Mo) on the corrosion behavior and scale protectiveness of carbon steel in CO₂-saturated (sweet) brine (0.5 M NaCl) environment, under hydrodynamic control, at 80°C in a slightly acidic environment (pH 6.6). The previous work used comparison with in-situ X-ray diffraction data to show that the current transient following an anodic potential step could be deconstructed into a part corresponding to dissolution through a thin amorphous surface film to form a colloidal product in solution, and a part that gave rise to a current peak that corresponded to the electrocrystallization of a scale on the surface, written as Reactions 1 and 2 below. The electrocrystallization part was described using an Avrami model, relating the fractional coverage of the surface to the volume of the growing crystalline phase. Growth was considered to occur directly at the interface with the rate controlled by the supersaturation at the interface:

\[
\text{Fe(s) + CO}_2^{2-} \rightarrow \text{FeCO}_3 \text{(crystalline) + 2e}^\text{−} \tag{1}
\]

\[
\text{Fe(s)} \rightarrow \text{Fe}^{3+} \text{(aq) + 2e}^\text{−};
\]

\[
\text{Fe}^{3+} \text{(aq) + CO}_2^{2-} \rightarrow \text{FeCO}_3 \text{(colloid)} \tag{2}
\]

The dissolution current (Equation 2) had two parts: a catalyzed dissolution, \(i_{\text{diss,cat}}\), that was diffusion controlled with Tafel dependence on electrode potential; and an un-catalyzed dissolution, \(i_{\text{diss,uncat}}\), that was flow independent and linearly dependent on electrode potential. The electrocrystallization current, Equation 1, was dependent on the surface supersaturation, which was controlled by Reaction 2. This proved to be a complex system where the coupling of Reactions 1 and 2, dependent on the electrode potential and solution flow rate, had a critical effect on the growth of the protective crystalline layer. Here, we use the same deconvolution of the chronoamperometric transient to demonstrate a remarkable effect of the addition of Mo to a Cr microalloyed steel that can be understood in terms of an effect solely on the kinetics of electrocrystallization. Scale morphologies are qualitatively characterized by scanning electron microscopy (SEM) and phases constituting the corrosion scales are identified using ex-situ X-ray Diffraction (XRD) analysis. Scale thicknesses were measured by transmission electron microscopy (TEM) imaging of sections of the corrosion scale prepared by Focused Ion Beam (FIB) sectioning in a dual-beam system. The results provide new insights into the mechanistic behavior of micro-alloying and enable design concepts for new steels with an optimized chemistry and very high durability-to-cost ratio to be developed.

### Experimental

**Materials.**—A number of different steel samples were used in this study: API J55 (0Cr0Mo) plain carbon steel, 1Cr0Mo, 1Cr0.2Mo, 1Cr0.7Mo, and 3.5Cr0.5Mo low alloy steels. The chemical compositions are shown in Table I. The microstructure changed from ferritic/pearlitic to martensitic with increasing Mo and Cr content: Figure 1. Samples were machined from pipeline samples to produce round bars of diameter 6 mm which were then customized to be used as rotating disk working electrodes (RDE). The samples were cut to 15 mm length pieces which were then inner-threaded from one end, ultrasonically cleaned with n-butane for 10 min, washed with distilled water and dried. The samples were then mounted using epoxy resin into a poly(tetrafluoroethylene) (PTFE) shield and, unless otherwise stated, the exposed surface was ground to a 15 μm finish using silicon carbide paper.

**Test solution.**—The base test solution for all experiments was 0.5 M NaCl, de-aerated and saturated with CO₂ by bubbling for at least 1 hour with a stream of high-purity CO₂ gas (supplier specification <4 ppm O₂) at 1 bar. The pH was altered by adding controlled amounts of 2 M NaOH (SI: table S1, Ref. 21), measured at room temperature with a laboratory pH meter and calculated at elevated temperature based on the equilibrium of ionic species in the solution with CO₂ at fixed partial pressure (data sources for carbonate equilibrium constants, water vapor pressure, Henry’s law constant for CO₂ and activity coefficients in aqueous NaCl as a function of temperature given in Ref. 30). An example calculation is given in the supplementary information (SI) of Ref. 21. This procedure was repeatable and reliable and avoided possible errors associated with the temperature correction of laboratory pH meters and temperature dependence of the reference element of combination pH electrodes. Experiments were conducted at 80°C and the calculated pH was 6.6. Over this range pHcalc,80°C = pHmeasured,RT ± 0.5. We note that dissolution of Fe could potentially cause a change in pH, however in these conditions is under static to quasi-static condition. The little information available in the literature under high flow conditions is often contradictory, mainly because of the different exposure conditions in terms of temperature and/or pH. Our previous work demonstrated that, at pH >6.5 and at 80°C, anodic dissolution of plain carbon steel to form a colloidal product proceeded in parallel with an anodic electrocrystallization reaction that resulted in a crystalline scale. The dissolution current and the surface supersaturation were shown to be controlled by the thickness of an initially-formed amorphous layer, the supersaturation being determined by the precipitation rate constant of colloidal FeCO₃ and by the product of the current for Fe dissolution and the diffusion boundary layer thickness. Traces of Cr⁺⁺ in the solution significantly accelerated the precipitation rate of the colloidal precursor and accelerated the appearance of the crystalline scale. Traces of molybdate in the solution also affected the rate of formation of crystalline spherulite.

### Table I. Bulk Composition of the Alloys: Chemical analysis provided by the vendor.

| Steel samples | Composition: wt% (and Fe bal.) |
|---------------|--------------------------------|
| Grades C Si Mn Cr Mo S P Ni Cu Al V |
| 0Cr. 0Mo      | 0.29 0.33 1.30 0.06 0.04 0.001 0.009 0.02 0.02 - 0.001 |
| 1Cr. 0Mo      | 0.52 0.38 0.67 0.94 - - 0.025 0.033 - - 0.165 |
| 1Cr0.2Mo      | 0.38 0.267 0.8 0.908 0.21 0.002 0.012 - - - - |
| 1Cr0.7Mo      | 0.28 0.23 0.30 1.05 0.7 0.001 0.008 0.03 0.06 - 0.045 |
| 3.5Cr0.5Mo    | 0.08 0.31 0.54 3.51 0.51 0.001 0.01 0.05 0.21 - 0.14 |

| Grades | C | Si | Mn | Cr | Mo | S | P | Ni | Cu | Al | V |
|--------|---|----|----|----|----|---|---|----|----|----|---|
| 0Cr. 0Mo | 0.29 | 0.33 | 1.30 | 0.06 | 0.04 | 0.001 | 0.009 | 0.02 | 0.02 | - | 0.001 |
| 1Cr. 0Mo | 0.52 | 0.38 | 0.67 | 0.94 | - | - | 0.025 | 0.033 | - | - | 0.165 |
| 1Cr0.2Mo | 0.38 | 0.267 | 0.8 | 0.908 | 0.21 | 0.002 | 0.012 | - | - | - | - |
| 1Cr0.7Mo | 0.28 | 0.23 | 0.30 | 1.05 | 0.7 | 0.001 | 0.008 | 0.03 | 0.06 | - | 0.045 |
| 3.5Cr0.5Mo | 0.08 | 0.31 | 0.54 | 3.51 | 0.51 | 0.001 | 0.01 | 0.05 | 0.21 | - | 0.14 |
measurements the room temperature pH measured before and after an experiment showed changes <0.01 pH unit.

Reference electrodes.—Reference electrode potentials are strongly temperature-dependent31,32 and with commercial electrodes there is a possible issue that, at elevated temperature the reference solution is not saturated in AgCl. In the laboratory cells, the reference electrode Ag,AgCl /sat. KCl was mounted externally and connected to the cell via a Luggin capillary containing the test solution. The temperature of the external reference electrode was measured to be around 40°C. The correction to the reference electrode at room temperature is +10 mV.32

Electrochemistry flow (RDE) experiments.—The apparatus is shown in the SI of Ref. 21. The electrochemical tests were carried out in a 1 L double-jacketed glass cell. Water was circulated through the outer jacket of the cell at a constant temperature. The experiments were controlled using an Gamry 600 Potentiostat. The counter electrode (CE) was a Pt wire ring in the plane of, and centered on the working electrode (WE). As noted above, the Ag,AgCl/sat KCl reference electrode was held externally and connected to the cell via Luggin capillary containing the test solution; the tip of the capillary was centered on the WE. The RDE was controlled using a Gamry RDE710 Rotating Electrode regulator. The experimental sequence was: (a) a potential of −1 V (vs. Ag,AgCl/sat KCl) was applied to the sample for 5 minutes to reduce air-formed surface oxides; (b) the open-circuit potential, \( E_{OC} \), was recorded until an apparent steady-state was reached (approximately 3–5 minutes). Once the desired condition was achieved, the CO₂ gas bubbler inlet was switched to the gas blanket arrangement; (c) an anodic potentiostatic step was applied to a fixed potential with respect to OCP and the resulting current density signal was recorded. Experiments were conducted at either fixed RDE rotational speed throughout the measurement, or stepping the rotation rate from high to low value and back again, each step being held for 1 minute. Throughout the experiment, the cell was sealed to prevent oxygen ingress, and CO₂ was bubbled or blanketed continuously. At the end of each run, the electrode was removed into the air, washed, dried and detached from the rotating disk assembly before X-ray diffraction patterns were recorded using a PANalytical Empyrean instrument with photon counting PIXcel³D detector.

Scale morphology, thickness and chemistry.—The morphology of the electrochemically treated samples with corrosion scales were analyzed using SEM (Quanta 650 from FEI operated at 10 kV), and scale cross-section by using the FIB lift-out technique in a dual-beam Helios NanoLab 600 from FEI. The scale thickness was measured from the cross-sectional samples in a JEOL-2100F TEM. Chemical analysis was performed using energy dispersive X-Ray (EDX) analysis in the TEM, using a beam voltage of 10 kV.

Results and Discussion

Representative potentiostatic current transients for low and high flow conditions are shown in Figure 2. The general current transient behavior shows that following the potential step from the open-circuit potential, \( E_{OC} \), the current density decreases rapidly to a plateau. After some time, it then rises to a peak indicating coverage of the electrode surface by a crystalline layer, as indicated in the figure, before decaying to a low value. By comparing the chronoamperometric behavior we hypothesize that the models for the plain carbon steel and the Cr/Mo micro-alloyed steels essentially follow the same pattern, with some modifications in their constituting components and that the variation depends on the type and level of micro-alloying.

Comparing the potentiostatic current-transient (Figure 2) of the non-alloyed carbon steels (J55) with that of the Cr/Mo micro-alloyed steel in this work, it is clear that micro-alloying with Cr induces a
reduction in the overall anodic current density passing through the corrosion scale. Our previous work has shown that the presence of Cr$^{3+}$ in solution$^{13,14}$ and of 1% Cr, 0.25% Mo in the steel$^{14}$ decreased the critical supersaturation for formation of siderite and increased the crystallization rate on the electrode. No significant effect of the presence of Cr alone in the steel is observed in the time to the current peak in Figure 2, implying that, in the present experiments, the effect on the crystallization rate of Cr in the steel, in the absence of Mo, was small. When we further compare the potentiostatic current transients of Cr micro-alloyed steel with combined Cr-Mo micro-alloyed steel, an additional effect of Mo is clearly observed; increasing Mo concentration in the steel results in a lower peak current and more rapid transformation to the protective crystalline phase. In fact, we observe that the introduction of 0.7 wt% Mo in 1Cr carbon-steel accelerates the film formation process, and at the same time reduces the overall current flux throughout the transient. Notably, for 1Cr0.7Mo steel the peak current density in the current transient (i.e. the crystallization peak) was observed even sooner than for the 3.5Cr0.5Mo steel which suggests the faster crystallization is the effect of higher Mo content. Overall, 1Cr0.7Mo steel induces accelerated crystallization and at the

Figure 2. Potentiostatic current-transient under three anodic over-potentials and two different flow rates (RPMs). Calculated$^{38,39}$ maximum IR drop was <10 mV.
same time reduces the overall current flux passing through the corrosion scale. 1Cr0.7Mo steel also seems eventually to attain passivation at a degree comparable to that of 3.5Cr0.5Mo steel.

Figure 2 shows that the effects of microalloying were extremely sensitive to electrode potential and electrode rotation rate. Figure 3 and Table II compare the steels at \( E = E_{OC} = +150 \text{ mV} \) and rotation rate 1000 rpm. The current density after 30 min, which can be used as an index for corrosion rate, shows a reduction by \( \sim 10 \) times for all the Cr/Mo micro-alloyed steels compared to the plain carbon steel. Figure 2 shows that in the lower flow regime (100 RPM) and at the same potential step (i.e. 150 mV above the OCP), the difference between the plain carbon steel and the Cr/Mo micro-alloyed steels was very significant: the plain carbon steel did not passivate on the time scale of the experiment whereas all the microalloyed steels showed a current steadily decreasing to a low value. At still lower potential, none of the steels showed current decreasing to a very low value on the time scale of the experiment.

In our previous work, we showed that the crystal growth rate constant correlates with the time to achieve the current peak in the potentiostatic transient, and hence deduced that the time to the peak can be used to deconvolute the dependence of the crystal growth rate on electrode potential and rotation rate. In addition, we developed the idea that scale formation is dependent on the surface supersaturation of ferrous carbonate (FeCO\(_3\)) controlled by transport rate, the dissolution overpotential. In general, the presence of Cr/Mo reduced the plateau current density before the crystallization peak, \( D \) the diffusion coefficient for Fe\(^2+\), \( c_{tot} \) the total concentration of carbon species and \( F \) is Faraday’s constant. The plateau current density refers to the portion of the current transient where the current density reaches a quasi-steady state after the potential step from \( E_{OC} \). This quasi-steady-state current continues until the crystallization current becomes significant. The experimental quantities \( t_{peak} \) and \( i_{plat} \) are derived from the data in Figure 2 and are given in Table II (in some cases are approximate). Figure 4 suggests that increasing Mo content makes the rate of crystallization significantly faster compared to the steels with less Mo content for similar surface dissolution flux of Fe\(^2+\). In contrast the effect of Cr at 1 wt% level was much less significant.

Figure 5 shows Levich plots for the plateau current density with rotation rate first decreasing (phase 1) and then increasing (phase 2). The growth of the crystalline layer with time causes the curvature and hysteresis in these plots, which is less marked at lower anodic overpotential. In general, the presence of Cr/Mo reduced the plateau current densities. Under relatively lower anodic overpotential (e.g. \( E_{OC} = 20 \text{ mV} \)), for the non-alloyed steel (155), the values of plateau currents during phase 1 and 2 were almost overlapping, presumably due to the absence of any crystalline layer. On the other hand, for Mo-containing steels, the hysteresis indicates the formation of a protective crystalline layer even at a very small anodic over-potential. These observations parallel the effects seen in Figures 2 and 3.

Following our previous work, \( \delta \) the rotation rate dependence of the plateau current is as follows:

\[
i_{plat} = k_n \omega^{\frac{1}{2}} + i_{dis,n} = i_{dis} + i_{dis,n}
\]

where \( i_{dis} \) denotes the transport-dependent part of the current, \( k_n \) is the Levich constant, \( \omega \) is the angular rotation rate of the electrode (rad.s\(^{-1}\)) and \( i_{dis,n} \) the potential dependent offset (mA.cm\(^{-2}\)). For the transport-dependent part it has been assumed that in the steady-state, dissolution of the pre-peak film occurs with a surface concentration, \( c_{s} \), of a dissolving species (assumed to be a carbonato- or bicarbonato-Fe(II) species\(^{3,14} \)) that is fixed just by the electrode potential. Here \( \gamma \) is the kinematic viscosity (3.80 \( \times \) 10\(^{-6}\) cm\(^2\) s\(^{-1}\) for 0.5 M NaCl solution at 80°C) and \( D \) the diffusion coefficient of the dissolving species. Levich slopes and intercepts were estimated from the initial measured as the reciprocal of the time to the current peak, \( t_{peak}^{-1} \), as a function of the deduced dimensionless surface dissolution flux of Fe\(^2+\), \( J = i_{plat}/2FDc_{tot} \) (where \( b \) denotes the diffusion boundary layer thickness calculated from the Levich equation for the rotating disc, \( i_{plat} \), the plateau current density before the crystallization peak, \( D \) the diffusion coefficient for Fe\(^2+\), \( c_{tot} \) the total concentration of carbon species and \( F \) is Faraday’s constant). The plateau current density refers to the portion of the current transient where the current density reaches a quasi-steady state after the potential step from \( E_{OC} \). This quasi-steady-state current continues until the crystallization current becomes significant. The experimental quantities \( t_{peak} \) and \( i_{plat} \) are derived from the data in Figure 2 and are given in Table II (in some cases are approximate). Figure 4 suggests that increasing Mo content makes the rate of crystallization significantly faster compared to the steels with less Mo content for similar surface dissolution flux of Fe\(^2+\). In contrast the effect of Cr at 1 wt% level was much less significant.
Figure 5. Rotation-dependent plateau current density ($i_{plat}$) vs (RPM)$^{1/2}$, where first RPM decreased from 3000 to 0 and then RPM increased from 0 to 3000 at regular intervals of time at three different anodic over-potentials.

linear part at high rotation rate of the plots in Figure 5, where it was assumed that the effect of the growth of the crystalline layer was small. Figures 6 and 7 show the electrode potential dependence of slope and intercept. Following the interpretation developed previously and implied by Equation 3, the uncatalysed dissolution rate, $i_{diss,n}$ is, within the accuracy of the measurements, independent of the Cr and Mo content of the alloy over the range investigated. The transport-dependent, catalyzed element of the dissolution current, $i_{diss}$, however appears to be significantly dependent on the Cr and Mo content of the alloy. The implication is that the surface concentration of the dissolving species for FeCO$_3$ is significantly dependent on the Cr and Mo content of the alloy. It is the diminution of the transport-dependent element of the dissolution current that is responsible for the decrease in surface flux and hence surface supersaturation with addition of Mo, that is seen in Figure 4.

Figure 8 shows the XRD patterns, measured ex-situ, after the experiments. The phases observed for the polished sample with no corrosion scale (labelled ‘no scale’: brown line) and for plain carbon steel...
Figure 6. The Levich slope as an index of surface concentration of the dissolving species for FeCO$_3$ vs. electrode potential. Levich slope is estimated from the rotation rate dependence of plateau current.

with corrosion scale (J55: blue line) scanning (1 h) from $2\theta = 10–70^\circ$ are indicated. The inset shows a 2 hr scan over $2\theta = 31–36^\circ$ to show diffraction peaks for the major phases observed for the corrosion scales on the different steels. In general, for both plain carbon steel and Cr/Mo micro-alloyed steels, the corrosion scales are composed of siderite and chukanovite. However with microalloying the relative amount of chukanovite appears to decrease, and the diffraction lines appear broader, implying smaller crystallite size. The results are consistent with an effect of microalloying on crystallization kinetics, which is different for chukanovite and siderite. We can also speculative relate this observation to our previous finding$^{21}$ where we have shown that the chukanovite to siderite ratio reaches a maximum in a pH range around 6.8 and reduces either side of this range. The local pH at the surface depends on the precipitation rate of the colloidal species$^{21}$ and the data indicate that the precipitation rate is affected not only by the addition of Cr (as in previous work$^{13,14}$) but also by the addition of Mo to the alloy: this might provide an explanation for the change in chukanovite: siderite ratio.

Figures 9 and 10 respectively show representative SEM images of the scale morphologies of different steels formed at 100 RPM and 1000 RPM at an anodic potential of +150 mV vs OCP. SEM images shown here are taken from the region close to the circumference of the sample where the circumferential velocity and consequent surface shear due to the rotating disk electrode would be greatest. A marked effect of both flow and alloy composition is shown. At the lower rotation rate (Figure 9) coverage of the surface by a microcrystalline layer is seen. With increased Cr or Mo, this layer becomes denser. At the higher rotation rate (Figure 10) for non-alloyed steel (J55) interlocking siderite crystals growing from different habit planes are observed. There are significantly fewer of such large crystals observable on the images for the Cr/Mo micro-alloyed steels. As well as the large crystals, there is a background of a microcrystalline mat, that appears to be more dense on the samples with higher Cr and Mo. The observations are consistent with the interpretation advanced above: if the crystal nucleation is more rapid for the Cr/Mo steels, the surface would become covered with very small crystals whereas a slower nucleation rate on the J55 steel compared to the crystal growth rate would lead to larger crystals. The crystals on the surface of the J55 are faceted, perhaps reflecting a different growth rate of different crystal planes and successive nucleation on to the growing crystals. This type of large, faceted siderite crystal is rarely observed in case of the Cr/Mo micro-alloyed steel.

Figures 11a and 11b are TEM images of FIB sectioned plain carbon (non-alloy) steel (J55: 0Cr0Mo) showing scale thickness of $\sim 1\ \mu m$ at 100 RPM and $\sim 1.5\ \mu m$ at 1000 RPM. Figures 12a and 12b are the TEM images of FIB sectioned micro-alloy steel (1Cr0.7Mo) showing scale thickness of $\sim 0.15\ \mu m$ at 100 RPM and $\sim 1\ \mu m$ at 1000 RPM respectively. The scales are significantly thinner than those reported at lower pH$^{15–19}$ and show a uniform distribution of Cr at a low concentration throughout the thickness with no evidence of Cr-clustering (Figure 13). Under the conditions that we have studied, there is no evidence for an amorphous discrete Cr(OH)$_3$ phase. The scale formed on J55 is found to be more porous compared to the scales formed on 1Cr0.7Mo; suggesting that the addition of Cr/Mo...
Figure 9. SEM images showing the morphology of the corrosion scales taken at the end of the electrochemical tests after water-rinsing and drying. Visible cracks are most likely a consequence of the drying. Conditions: anodic over-potential: $E_{OC} + 150$ mV, pH: 6.6. Temp: 80°C, Flow rate: 100 RPM.

causes formation of a denser scale which is relatively thinner but renders either similar (at lower flow condition) or better (at higher flow condition) degree of protectiveness as indicated by the current density.

Our previous results have shown a significant effect of the role of Cr$^{3+}$ in solution on the electrocrystallization rate of siderite, and also an effect of molybdate in solution.\textsuperscript{13,14} The present work has shown a marked acceleration of electrocrystallization associated with Mo in the alloy. It has also shown an effect on the surface chemistry of dissolution to the colloid. Our data also show that, in the presence of both Cr and Mo, the crystalline surface scale formed is thinner and more protective, with smaller crystallites. Whilst there might be an effect associated with the change of microstructure,\textsuperscript{20} these observations lead us to presume that the presence of Mo makes the critical size of stable nuclei (which is a precursor to the crystal development process) relatively smaller and hence induces a faster crystallization and development of a protective scale consisting of smaller size crystallites. A possible mechanism is that of colloid-mediated crystal assembly or of organized attachment mediated by solution species, from an amorphous precursor or cluster.\textsuperscript{35,36} The demonstration of a synergistic effect of Cr and Mo would require the study of alloys without Cr, and these were not available to us. However, at elevated temperature, molybdo-chromate heteropolyacids form in aqueous solutions containing chromium and molybdenum.\textsuperscript{37} It is a speculation that such species could act as catalysts for the crystal assembly.

Conclusions

Electrochemical measurements during scale formation on micro-alloyed steels in a sweet environment show evidence of faster scale crystallization with increasing concentration of Cr and Mo. Cross-sectional TEM imaging of the scales confirmed the scale thickness of Cr/Mo micro-alloyed steel (e.g. 1Cr0.7Mo) is an order of magnitude thinner, but confers better protectivity when compared to their non-alloyed counterpart.

The passivation kinetics of 1Cr0.7Mo and 3.5Cr0.5Mo steels appeared to be comparable even though the initial current density was relatively lower for 3.5Cr0.5Mo, indicating a promising interaction between Cr and Mo and leading to the idea that an optimized addition of Mo might replace a much higher percentage of Cr for a similar degree of corrosion protection.
From a mechanistic perspective, we suggest that the addition of small amounts of Cr/Mo modulates the current due to dissolution of iron, as well as the current due to growth of a crystalline layer. We suggest that Cr/Mo species in solution at the metal interface significantly accelerate electrocrystallization of siderite. A possible mechanism is that of colloid-mediated crystal assembly or of organized attachment mediated by solution species, from an amorphous precursor or cluster.
Figure 12. TEM image of FIB sectioned micro-alloyed steel (1Cr 0.7Mo) showing scale thickness at (a) 100 RPM (measured avg. scale thickness: 0.15 μm), (b) 1000 RPM (measured avg. scale thickness: 1 μm). The sample was Pt-capped before sectioning, $E_{OC} + 150$ mV, 30 min.

Figure 13. EDX mapping from scale cross-section formed on 1Cr.0.7Mo steel at 1000 RPM, $E_{OC} + 150$ mV, 30 min, showing uniform distribution of Fe and Cr within the scale.

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