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Usefulness of In-Situ Synchrotron Study on Scale Formation during CO₂ Corrosion of Mild Steel: A Review

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Despite the availability of the detailed knowledge about the chemical, electrochemical and transport processes associated with the formation of ferrous carbonate during CO₂- corrosion of mild steel, information available about the mechanism of early nucleation stages of FeCO₃ (siderite) film formation was only speculative. In depth knowledge related to the early stage nucleation of siderite scale and its subsequent development and gradual growth were revealed only recently by judicious exploration of in-situ synchrotron based experimentation. Moreover, application of in-situ synchrotron x-ray diffraction technique rendered ability to monitor the gradual real time growth of FeCO₃ scale with the efficacy of simultaneous controllability of the corrosion conditions electrochemically. This work shades light on how in-situ synchrotron study revealed apparent mysteries related to formation & growth of siderite scale during CO₂- corrosion of mild steel.

Keywords

In-situ synchrotron, CO₂-Corrosion of mild steel, Nucleation mechanism during CO₂- corrosion.

Figure 1 (a) and (b) illustrate the photograph and schematic of experimental set up for in-situ synchrotron X-ray diffraction experiments using the powder diffraction Australian beam line.

Figure 2 shows the anodic current as a function of time in a potentiostatic test in the NaCl solution at pH 6.3 (pCO₂ = 1bar) and an applied potential of -500 mV (vs SCE), together with the intensities of the Fe and FeCO₃ signals from the in-situ synchrotron XRD [1]. There is a clear peak in the current transient, with the XRD results showing FeCO₃ formation during the increasing portion of this transient and then a rapidly decreasing rate of FeCO₃ formation as the anodic current decreases towards the end of the test, indicating the growth of a protective surface scale. In these studies, it is shown that siderite only forms once the critical super-saturation is exceeded within a defined

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boundary layer and that the steel microstructure has critical role in developing a surface texture within which the critical super-saturation could develop. This idea of siderite nucleation in solution with a critically saturated boundary layer close to the metal surface is unlike the heterogeneous nucleation and growth phenomenon which occurs directly on the surface via solid state formation [1]. Establishment of this ideology was able to resolve the apparent thermodynamic anomaly observed in practice.

One of the apparent thermodynamic anomalies in CO_2 - H_2S mixed system is couched on the fact that in spite of the higher (~3 time) aqueous solubility of H_2S compared to CO_2 under similar temperature and pressure conditions, the formation of iron sulfide has been observed to be faster and predominant over iron carbonate under most parametric conditions even at a trace level of H_2S concentration in CO_2 - H_2S system. This fact indicates the formation of iron sulfide and iron carbonate films to be regulated by different mechanisms. In-situ synchrotron study revealed the early stage nucleation of iron carbonate (siderite) film and indicated that to be a gradual process giving rise to the formation of crystalline siderite phase only after the critical supersaturation stage is reached. Given that, there is significant time lag between the start of supersaturation and critical supersaturation limit, there is a possibility for iron sulfide formation during that time lag, as it forms by solid state formation mechanism which is a faster process. It is the in-situ synchrotron study which made it possible to illustrate the appreciable time lag between the start of supersaturation and critical supersaturation limit.

Ingham et al. [2] used in-situ synchrotron small- and wide-angle X-ray scattering (SAXS and WAXS) to demonstrate that the formation of crystalline siderite (FeCO_3) during the corrosion of steel in CO_2 -saturated brine is actually preceded by the formation of a colloidal precipitate and an amorphous surface layer, both assumed to be amorphous ferrous carbonate. Grazing incidence SAXS showed that upon the application of an anodic potential, film forms instantaneously and then a separate population of particles develops in the later stage followed by the formation of the ultimate crystalline FeCO_3 , observed by WAXS. Ingham et al. [2] interpreted these observations in terms of crystal nucleation within the amorphous surface layer. This observation was speculated to bear a significant consequence on the morphology of the corrosion scale and hence its protectiveness. However, it would be important to understand the effects of local pH change as well as variation in temperature in this gradual formation and development of siderite scale and then to find out a quantitative correlation of this process with the mentioned parameters.

The fact of stable, adherent and protective siderite film formation in presence of trace amount Cr^{3+} was known [3, 4]. However the associated mechanism was not clearly understood until in-situ synchrotron x-ray diffraction study revealed a clearer picture of the mechanistic aspect of the expedited siderite film formation in presence of traces of Cr^{3+} [2, 5]. This recently done in-situ synchrotron study made it clear that traces of Cr^{3+} in the solution significantly expedites the precipitation rate of the colloidal precursor and thus accelerate the appearance of the crystalline scale through its catalyzing influence on the nucleation process by modulating the local pH level at the steel surface and thus reducing of the critical supersaturation for precipitation.

Another interesting and critical factor in developing surface texture within which the critical supersaturation can be developed is steel microstructure. Consequently, steel microstructure must have intimate relationship with the corrosion process and morphology of the scale as microstructure can change the diffusion conditions at the steel surface affecting the local supersaturation of siderite. However, in-depth mechanistic information related microstructural effect on adherent and protective scale formation was hardly available in the literature. It is recommended to perform in-situ synchrotron X-ray diffraction experiment in order to make a detailed investigation of such a phenomena. Ko et al [6] recently conducted such a study in order to investigate the effect of microstructure and boundary layer conditions on CO_2 corrosion of low alloy steels. This recent investigation clearly demonstrated that the nucleation of crystalline scales onto the surface of steels under CO_2 corrosion at elevated temperature is critically dependent on the initial surface roughness, microstructure-related surface roughness developed during corrosion. This study also indicated the interdependence between microstructure and chromium-enhanced siderite nucleation. However, finding out the quantitative effects of surface roughness on the initial nucleation process (rate) of the scale as well as the stability of the scale would be a good addition to this study.

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