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СОВРЕМЕННОЕ СОСТОЯНИЕ И ПРОБЛЕМЫ СЕРОВОДОРОДНОЙ КОРРОЗИИ МЕТАЛЛОВ В РАСТВОРАХ ЭЛЕКТРОЛИТОВ

© С.Е. Симонина, В.Н. Вигдеревич

Simonina S.E., Vighderovich V.N. The modern state and problems of sulphur-hydrogen corrosion of metals in the electrolytic solutions. Some problems of sulphur-hydrogen corrosion as H^+ cathode reduction theoretical aspects, peculiarities of H_2S -corrosion, total regularities of the corrosion inhibitors action, protection at the presence of hydrogen sulphide are considered in the article.

ВВЕДЕНИЕ

Сероводородная коррозия – одна из наиболее серьезных причин коррозионного разрушения при эксплуатации оборудования в широком диапазоне сред и условий. Содержание сероводорода в обводненной нефти некоторых нефтяных скважин достигает 500 мг/л. Сероводород обладает уникальными агрессивными свойствами и вызывает коррозионное повреждение оборудования в результате электрохимической, а также, как и хлоридной, коррозии и водородного осыпания. Коррозия металлов в кислых и сероводородных средах протекает в основном с катодной депротонизацией, поэтому большой интерес представляет изучение механизмов и кинетики реакции катодного выделения водорода (РВН).

ТЕОРЕТИЧЕСКИЕ АСПЕКТЫ КАТОДНОГО ВЫДЕЛЕНИЯ ВОДОРОДА

Механизм катодного восстановления доноров протонов, выражаемый, в частности, суммарной реакцией

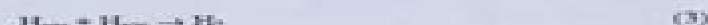


детально анализируется во многих монографиях и обзорах [1–7].

Процесс может протекать через медленные стадии – разряда (реакция Фольмера)



– рекомбинации (реакция Тейфеля)



– электрохимической десорбции (реакция Гейровского)



Суммарную реакцию можно представить как комбинацию любых двух стадий (2) – (3) или (2) – (4).

В механизме Фольмера – Тейфеля лимитирующей может выступить как стадия разряда, так и рекомбинация. В механизме Фольмера – Гейровского лимитирующей может быть либо разряд, либо электрохимическая десорбция. Согласно [6, 8], на железе лимитирующей является реакция (3), но [9, 10] – стадия (4).

Для условий замедленного разряда в условиях энергетически однородной поверхности получены зависимости [1]:

$$\varphi = \text{const}_1 + \frac{2RT}{\alpha F} \ln C_{H_3O^+} - \frac{1-\alpha}{\alpha} \Psi_1 - \frac{RT}{\alpha F} \ln i_a \quad (5)$$

$$\eta_H = \text{const}_2 - \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln C_{H_3O^+} + \frac{1-\alpha}{\alpha} \Psi_1 + \frac{RT}{\alpha F} \ln i_a \quad (6)$$

Лимитирующей стадией электрохимической десорбции соответствуют уравнения:

$$\varphi = \text{const}' + \frac{2RT}{(1+\alpha)F} \ln C_{H_3O^+} - \frac{RT}{(1+\alpha)F} \ln i_a \quad (7)$$

$$\eta_H = \text{const}'' - \frac{1-\alpha}{1+\alpha} \frac{RT}{F} \ln C_{H_3O^+} + \frac{RT}{(1+\alpha)F} \ln i_a \quad (8)$$

Для замедленной рекомбинации получены зависимости:

$$\varphi = \text{const}_3 + \frac{RT}{F} \ln C_{H_3O^+} - \frac{RT}{2F} \ln i_a \quad (9)$$

$$\eta_H = \text{const}_4 + \frac{RT}{2F} \ln i_a \quad (10)$$

Данные уравнения позволяют оценить теоретические величины кинетических параметров катодного восстановления ионов водорода, что дает возможность судить о механизме реакции [11].

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