Review

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Recent progress on the corrosion behavior of metallic materials in HF solution

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Abstract: Hydrofluoric acid (HF) or fluoride ion corrosion issues are often encountered in many fields, which have attracted extensive research due to its strong corrosiveness. In this paper, a critical review is presented based on recent progress on HF corrosion. In view of the discrepancy of fluoride ion compared with other ions, the special attack characteristics of fluoride ion are firstly discussed. Afterwards, the corrosion mechanisms of stainless steels, nickel-based alloys, and titanium alloys in HF solution or fluoride ion-containing environment are reviewed, and three typical corrosion behaviors are summarized, which are essentially weakening process of passivation of metallic materials. The effects of influencing factors (e.g. alloying elements, environmental factors, and stress, etc.) on HF corrosion are also discussed, which involve changes in passivation mechanism, the influence of HF attack mode and multiple damage mechanisms due to mechanical–chemical coupling. Finally, future research works on HF corrosion are proposed.

Keywords: corrosion mechanism; hydrofluoric acid (HF); nickel-based alloys; stainless steel; stress corrosion cracking; titanium alloys.

1 Introduction

Hydrofluoric acid (HF) is a special acid. Compared to strong corrosive medium (hydrochloric acid (HCl), nitric acid

(HNO₃), sulfuric acid (H₂SO₄), etc.), although HF belongs to weak acid with positive pK_a (3.17) (Ayotte et al. 2005; Perrin 1969), its corrosiveness is not inferior to strong acids (Jang et al. 2009a,b). It can severely corrode metals (except most noble metals such as gold and platinum, etc.) and substances bearing silicon (such as glass). The corrosion issue of HF has been investigated in many fields (Barnes 2000), such as fluoride chemical industry (Schillmoller 1998a,b), alkylation process (Hashim and Valerioti 1993), dental implantation (Guidi et al. 2012; Li et al. 2018), the IV generation molten salt reactor (Guo et al. 2018), nuclear spent fuel reprocessing process (Nagano et al. 1995), and car wash industry (Genuino et al. 2012), as shown in Figure 1. Especially in fluoride chemical industry, hydrogen fluoride is an important raw material for the production of fluorine chemical products. As water is inevitable during production process, HF solution is formed and results in corrosion of metallic materials. Thus, it is necessary to reasonably choose suitable materials as structural components to ensure safety during production.

In HF environments, corrosion issues include general corrosion and local corrosion that can reflect the corrosion resistance of materials. In addition, stress corrosion cracking (Rebak 2000) and corrosion fatigue (Roselino Ribeiro et al. 2007) caused by the presence of stress were also reported. In the past several decades, there were several reviews which focused on the evaluation of corrosion resistance of various alloys in HF solution. In 1993, Schillmoller published lots of corrosion rate and some stress corrosion cracking data of high Ni stainless steels (SS) and nickel-based alloys in HF solution, which provided a crucial basis for material selection (Schillmoller 1993). In 2001, Jennings (2001) reviewed the corrosion data and degradation information of materials exposed to anhydrous hydrofluoric acid (AHF) and HF solution with other acids and impurities. In addition, some standard and criterion are also released to address HF corrosion issue. National Association of Corrosion Engineers (NACE) published NACE 5A171 in 2007, which introduced the material for storing and handling aqueous HF and AHF. In the same year, the API RP 751 published by the American Petroleum Institute (API) summarized possible corrosion failure of

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equipment during alkylation process and provided corresponding recommendations and guidance. Although previous work includes a large amount of corrosion data of metals and its alloys in HF solutions, the corrosion behavior and internal mechanism are rarely mentioned. The understanding of the internal corrosion behavior and failure mechanism is not only helpful for material selection and design, but also plays an important role in formulating strategies to mitigate corrosion issues. Moreover, about 20 years had passed since the review of Schillmoller (1993) and Jennings (2001), and some advanced characterization methods (scanning electronic microscopy (SEM), transmission electron microscope (TEM)) and composition analysis techniques (energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-OES), etc.) have been extensively developed and applied. With the help of these advanced methods and techniques, not only the corrosion performance of more metallic material in HF solution was tested, significant progress on the corrosion behavior and mechanism were also made. It is the aim of this work to summarize progress in the past two decades.

In this review, the particularity of fluoride ion and its unique attack behavior are firstly discussed. Then, the corrosion behaviors and mechanisms of several metallic materials (e.g. austenitic stainless steels, nickel-based alloys, and Ti and its alloys) in HF solution are presented. In terms of alloy elements, the relationship between chemical composition (Mo, Cr, Fe, and Cu elements) and corrosion resistance in HF solution is discussed. In particular, questions such as how Mo affects the corrosion of alloy and whether Mo element is always protective are explored. With respect to the effect of environmental factors on HF corrosion, the internal attack modes of HF solution are shown, and the influence of stress is also taken into account. Finally, the perspectives for HF corrosion are proposed.

2 The attack characteristics of fluoride ion

2.1 The active dissolution capacity of fluoride ion

For most metallic materials, such as stainless steels, nickel-based alloys, and Ti alloys, etc., they were likely to be passivated when encountered acidic medium, such as HCl, H₂SO₄, and HNO₃, etc. (Daoud et al. 2014; Guo et al. 2020; Khan et al. 2020; Kim et al. 2011; Liu et al. 2017; Michiuchi

et al. 2006; Ningshen et al. 2011; Panossian et al. 2012; Ravi Shankar and Kamachi Mudali 2013; Sanni et al. 2019; Saravanan et al. 2019; Sarvghad et al. 2019; Sun et al. 2018). The passive film formed on surface aims to prevent the attack of corrosive ions. However, in HF solution or solutions mixed with fluoride ion, the passivation range is greatly shortened, which is ascribed to the active dissolution ability of fluoride ion. This point is supported by numerous electrochemical data and chemical composition results. Lochel and Strehblow (1983) pointed out that HF accelerated the transfer of oxides into fluorides on iron surface in order to damage passive film in 1M HClO₄ solution containing 0.1 M HF. Dai et al. (2020a) measured the corrosion rate of Q345R carbon steel in 40 wt% HF solution at room temperature, and the corrosion rate was also almost constant with immersion time, indicating the successively degradation of matrix. Similarly, controlled by active dissolution of fluoride ion, the passivation state of metal tended to dissolve with the addition of fluoride ion. As shown in Figure 2a and 2b, the protective film formed on pure Ti and Ti alloys in fluoride-containing sulfuric acid solution could be severely destroyed when fluoride ion concentration exceeded a critical value (for pure Ti, the critical value was 0.0005 M; for Ti alloys, this value increased) (Wang et al. 2016). In terms of mixture solution containing small amount of fluoride ion, only the concentration of fluoride ion up to threshold value could attack the passive film (Li et al. 2001). In addition, the passivation region of 904L SS was greatly reduced with HF concentration increasing from 0.1 to 10 M, and electrochemical impedance spectroscopy (EIS) results showed that the resistance of passive film increased by 94% (Zou et al. 2018). The active dissolution of fluoride ion damages the passive film in two ways. One is to make the compact passive film porous, and the other one is to form semisoluble fluorides through fluoridation, thinning the passive film.

2.2 The strong affinity of fluoride ion

The strong affinity of fluoride ion resulted from its largest electronegativity of 4.0 and the lowest polarizability of $0.81 \times 10^{-30} \text{ m}^3$ (Schmitt et al. 2004). Compared to other halide ions (e.g. Cl⁻, Br⁻, and I⁻), fluoride ion in the solution strongly attracted other ions and molecules, and at the same time promoted the polarization of other substances and aggravated their dissolution (Trompette 2015). It is believed that this is the essence of fluoride ion showing an active dissolution ability. In some fluoride ion-containing mixtures solution, the preferred affinity of fluoride ion is

Figure 1: The field of HF corrosion issues (pictures are obtained from the Internet).

always prominent, resulting in greater competitiveness with other ions, especially in acidic conditions. Wang et al. (2015a,b) found that the electrochemical behavior of pure Ti in 0–0.05M Na_2SO_4 with 0–0.05M NaF at pH 1.0–5.0 was completely controlled by the concentration of fluoride ion in solution, and the stability and integrity of passive film was directly affected by the invasion of fluoride ion. When multiple ions were mixed, the passivation degradation of 316L and pure Ti in H_2SO_4 solutions with various content of F^- (0, 0.5, and 5 mM) and Cl^- (0, 10, 600 mM) would be driven with the concentration of fluoride ion. It was also proved that Cl^- played a synergistic role to promote the attack by fluoride ion, and enhanced the affinity property of fluoride ion (Wang et al. 2018). It appears that the strong affinity of fluoride ion makes the material vulnerable to be corroded by fluoride ion, even in some mixed environments. But for some special corrosive environments, the

strong affinity of fluoride ion has a positive effect on the improvement corrosion resistance of the material. In concentrated sulfuric solution at high temperature, the presence of small amount of fluoride ion was beneficial for 304 SS, 904L SS and 2507 duplex SS (Yu et al. 2017), and corrosion potential increased with the addition of 6% NaF, which resulted from the preferential affinity between matrix and fluoride ion instead of S^{2-} . A layer of stable substance formed by the preferred affinity of fluoride ion inhibit attack from other corrosive media (Mason and Rittenhouse 1958; Stypula et al. 2009; Takeuchi et al. 2010; van der Merwe et al. 2016, 2020).

2.3 The overall corrosion and local corrosion of fluoride ion

The attack form of HF or fluoride ion was long considered to be comprehensive, namely uniform corrosion, which was associated with the overall attack of fluoride ion (Copson and Cheng 1956; Genuino et al. 2012; Jennings 2010; Qiu et al. 2020; Rebak 2000; Schillmoller 1998a,b; Seastrom 1964; Yu et al. 2015). However, local corrosion induced by HF or fluoride ion can still be seen from many studies. Table 1 summarizes these local corrosion situations. The local corrosion in HF solution or fluoride ion environment can be classified into two types, one is pit corrosion and another one is intergranular corrosion (IGC).

In terms of the cause of pitting, one is the precipitation inside the material. Li et al. (2014) reported that a Mo-rich μ phase in Ni–Cr–Mo alloy would induce pit due to local galvanic effect caused by the precipitation in HF solution. Moreover, the (Ti, Nb) (C, N) inclusion that did not react with HF solution in Inconel 600 would peel off under the uniform thinning of HF and destroy surface product, resulting in the appearance of pits (Dai et al. 2020a). While

Figure 2: (a) The open circuit potential (OCP) of Ti alloys in H_2SO_4 solutions containing fluoride ions, (b) is the OCP measurements of the first 1 h in (a) (Wang et al. 2016; copyright 2016, with permission from Elsevier).

Table 1: The corrosion forms of metal material in HF or fluoride ion-containing solution.

Material	Test method	Solution	Condition	Time	Corrosion forms	Main cause	References
Ti alloys	Electrochemical test	Fusayama artificial saliva containing 0.1% KF/NaF	pH = 6.15–3.0, room temperature	24 h/100 h	Pitting corrosion	The local destruction of passive film	Reclaru and Meyer (1998)
Fe and Ni	Electrochemical test	Phthalate buffer +0.1 M KF	pH = 5.0	–	Pits were only found on Fe	The local destruction of passive film	Strehblow et al. (1979)
Fe	Electrochemical test	1 M HClO ₄ + 0.1 M HF	pH = 5.0, 25 °C	2 h	Pitting corrosion	The local destruction of passive film	Löchel and Strehblow (1983)
Zr-based bulk metallic glass (Zr ₅₂ Al ₁₀ Ni ₆ Cu ₃₂)	Electrochemical test	0.1 M NaF	pH = 7.0 room temperature	–	Uniform corrosion	The overall attack of fluoride ion	Qiu et al. (2020)
Tin	Electrochemical test	0.1 M NaF	pH = 5.7, 10; room temperature	–	Pitting corrosion	The localized breakdown of passive film by fluoride ion with strong electric filed	Trompette (2015)
Q345R	Immersion test	40 wt% HF	Room temperature	2–72 h	Uniform corrosion with some pits	The uneven distribution of surface product and the escaping of hydrogen gas	Dai et al. (2020a)
316L SS	Immersion test	10–40 wt% HF	Room temperature	24 h	Uniform corrosion with some pits	The uneven distribution of surface product and the escaping of hydrogen gas	Chen et al. (2020a,b)
Inconel 600	Immersion test	40 wt% HF	50 °C	24–168 h	Uniform corrosion with pitting corrosion	The inclusion of (Ti, Nb) (C, N)	Dai et al. (2020b)
Hastelloy C-276	Immersion test	40 wt% HF	50 °C	24–168 h	Uniform corrosion with intergranular corrosion	The intergranular M ₆ C	Dai et al. (2020b)
Monel 400	Immersion test	40 wt% HF	50 °C	24–168 h	Uniform corrosion	The overall attack of HF	Dai et al. (2020b)
Ni–30Co–16Cr–15Mo alloy	Immersion test	5.2 M HF	100 °C	1–100 h	Slight intergranular corrosion	The weak protection of product in intergranular area	Zhang et al. (2014a,b)
Ni–16Cr–15Mo alloy	Immersion test	5.2 M HF	100 °C	1–100 h	Pitting corrosion	The precipitation of μ phase	Li et al. (2014)
Ni–30Co–16Cr–15Mo–6Fe alloy with Cu addition	Immersion test	5.2 M HF	100 °C	1–100 h	Slight intergranular corrosion	The precipitation of Cu-riched phase	Yang et al. (2020a,b)
Ni–Co–Cr–Mo alloy	Immersion test	5.2 M HF	100 °C	1–100 h	Slight intergranular corrosion	The weak protection of product in intergranular area	Hou et al. (2015a,b)

another mechanism of pits formation is associated with the strong active dissolution of fluoride ion. The severe degradation on Q345R and 316L SS induced by HF made surface products accumulate randomly on surface. Besides, the intense redox reaction between matrix or passive film and HF solution could generate abundant hydrogen gas. It was these two reasons that caused pit formation at local area where the chemical reaction was intense (Chen et al. 2020a,b; Dai et al. 2020a). Strehblow and Marcus (2002), Strehblow et al. (1979), and Trompette (2015) proposed a special pits formation process in fluoride ion environment. The passive film on tin was thinned by the overall attack of fluoride ion in $\text{pH} > 5$ environment, and the weak area of the thinned passive film would rupture when subjected to the strong electric field of fluoride ion with the highest surface charge density (Trompette 2015), giving rises to pits.

Similarly, the intergranular precipitation was prone to induce severe IGC due to the elemental discrepancy between grain boundary and its surrounding area in HF or fluoride ion-containing solution (Osborne 2002; Yang et al. 2020a,b). Some researches (Hou et al. 2015a,b; Yang et al. 2020a,b; Zhang et al. 2014a,b) also pointed out that the attack by HF solution at grain boundary was slightly severe than interior grain. As a result, the surface product covered on intergranular was more likely to crack, and the exposed area was more heavily attacked. In all, the corrosion forms of metallic materials in HF or fluoride ion-containing solution have many types. When analyzing the corrosion form, not only the attack behavior of fluoride ion should be considered, the microstructure inhomogeneity of materials and the interaction between passive film and fluoride ion during corrosion cannot be neglected as well (Figure 3).

3 Corrosion mechanisms of metallic materials in HF or fluoride ion-containing environment

3.1 Austenitic stainless steels

Austenitic stainless steel is a typical Fe–Cr–Ni alloy. Compared with carbon steels, the iron content is reduced, and the addition of other metallic elements (Cr, Ni, and Mn, etc.) significantly promotes corrosion resistant of SS. It was the noble elements that weakened corrosion sensitivity by accelerating passivation and the formation of beneficial passive films (Olsson and Landolt 2003).

As described in Section 2.1, fluoride ion shows intense active dissolution ability. It has been proved that the underlying corrosion mechanism of austenitic SS is passivation degraded process in HF or fluoride ion solution. But there are two different views about the weakening process of austenitic SS passivation. From the perspective of reaction kinetics, the corrosion mechanism of SS in HF solution can be described as the diffusion between metal elements (e.g. Ni, Cr, and Mo, etc.) and medium (HF and H_2O). As shown in Eqs. (1)–(3), three typical anions coexist in HF solution, F^- , O^{2-} , and OH^- . Some scholars believed that metallic cations were prone to react with O^{2-} and OH^- to generate a passive film layer on surface (Bastidas et al. 1997; Bond and Taylor 1970; Chen et al. 2020a,b; Kocijan et al. 2011; Li et al. 2001; Löchel and Strehblow 1983; Mack 1995; Strehblow et al. 1979; Wang et al. 2018; Yang et al. 2010, 2012), as expressed in Eqs. (1) and (2). When compact passive film was preferentially formed on surface, free fluoride ion in solution would accumulate on passive film quickly and evenly, followed by reacting with these oxides as expressed by Eq. (4) (Strehblow et al. 1979). The products generated by Eq. (4) belonged to soluble or semisoluble substances (Wang et al. 2018). Under the continuous attack of fluoride ion, the passive film became thinner, while surface products continued to thicken and gradually evolved into a porous morphology. It was the destruction by these fluoride ions that led to the gradual loss of passive film, as schematically shown in Figure 4a. This mechanism

Figure 3: The corrosion forms in fluoride ion environment and its causes.

Two corrosion mechanism of austenitic SS in HF or fluoride ion-containing solution

Figure 4: (a, b) Two different corrosion mechanisms of stainless steel in HF solution: (a) Describes the degradation process of surface passive film induced by fluoride ion, while (b) depicts fluoride ion preferential affinity inhibit the passivation process. These two graphs were drawn based on the research of Wang et al. (2018) and Zou et al. (2018).

can be regarded as fluoride ion induced passive film degradation process.

However, other scholars proposed that the degradation of passive film was due to the preferential affinity between F^- and matrix (Jiang et al. 2019; van der Merwe et al. 2020; Yu et al. 2015, 2017; Zou et al. 2018), as shown in Eqs. (1) and (3). The formed fluorides on surface severely inhibited the passivation process of austenitic SS, but a narrow passivation region could be still detected in polarization curve. Zou et al. (2018) pointed out that free fluoride ion in solution were depleted during corrosion process, which resulted in increased cavities in surface fluorides. Afterwards, H_2O , O^{2-} , or OH^- penetrated into fluoride and reacted with the bottom of matrix to form a passive film at the interface between matrix and fluorides. The above process is schematically shown in Figure 4b, which was a process of preferential affinity of fluoride ion to matrix to inhibit passivation. These two mechanisms were opposite processes.

where M is metallic elements, n is the charge number of electron.

3.2 Nickel-based alloys

Nickel-based alloys were composed of Ni (>50 wt%) mixed with small amount of other elements (Sarmiento Klapper et al. 2017). Compared to SSs, the corrosion resistance of nickel-based alloys was excellent. Due to the strong corrosiveness of HF solution, nickel-based alloys were increasingly used to replace stainless steels and carbon steels as key components material (Rebak 2000). Unlike SSs, nickel-based alloys are not only made of Ni as the main composition, but also contains different kinds of metallic elements (Cr, Mo, Cu and Fe, etc.). They can be divided into Ni-Cu (Monel 400), Ni-Mo (Hastelloy B-3), Ni-Cr-Mo (Hastelloy C-276, Hastelloy C-22, Haynes 242 and Haynes 625), and Ni-Cr-Fe (Inconel 600, Hastelloy G30) according to their chemical composition (Table 2). These alloys had different corrosion sensitivities in HF solution due to the discrepancy in elemental type and content (Yang et al. 2020a,b).

The corrosion mechanism of only three types of nickel-based alloys in HF solution were investigated, including Ni-Cr-Mo, Ni-Cr-Fe, and Ni-Cu alloys (Crook et al. 2007; Hou et al. 2014, 2015a,b; Li et al. 2014, 2015; Osborne 2002; Rebak et al. 2001; Yang et al. 2020a,b; Zhang et al. 2014a,b). The corrosion of these alloys in HF solution can be regarded as a weakening process of passivation. The source of weakening was the same as SSs, which was the invasion of fluoride ion (Li et al. 2015). However, the difference lies in that the fluoridation and oxidation cannot be separated for

Table 2: Chemical composition of various nickel-based alloys (wt%) (Hou et al. 2014, 2015a,b; Li et al. 2014; Pawel 1994; Yang et al. 2019).

Composition	Ni	Fe	Cr	Mo	Cu	C	Si	Mn	W
Monel 400	67	1.2	–	–	31.5	–	–	–	–
Hastelloy C-22	59	3	22	13	–	–	–	–	3
Hastelloy C-22HS	61	2	21	17	0.5	0.01	0.08	0.8	1
Hastelloy G30	44	15	30	5	2	–	–	–	2.5
Hastelloy G35	58	2	33.2	8.1	0.3	0.05	0.6	0.5	0.6
Haynes 625	61	2.5	21.5	9	–	0.05	0.2	0.2	–
Hastelloy C-276	57	–	15–16	15–16	–	–	–	0.0754	4
Hastelloy C-2000	59	–	23	16	1.5	–	–	–	–
Hastelloy B-3	65	1.5	1.5	28.5	–	–	–	–	–
Inconel 600	76	8	15.5	–	–	–	–	–	–
Haynes 242	65	–	8	25	–	–	–	–	–
Ni–Cr–Mo	Base	6	16	11	2	–	–	–	–

nickel-based alloys in HF solution. Yang et al. (2020a,b) and Li et al. (2014) pointed out that fluoride ion as a small part participated in the passivation process of Ni–Cr–Mo alloy with Cu in HF solution, and existed in passive film in the form of copper fluoride. Similarly, some Ni, Cr, and Fe fluorides could also be detected in surface passive film (Hou et al. 2014; Li et al. 2014). It suggested that the surface passive film of nickel-based alloys during HF corrosion was not only composed of metallic oxides, but also some stable fluorides. In addition, it meant that fluoride ions were not always detrimental in corrosion of nickel-based alloys. Its internal corrosion behavior can be described as the synergetic effects of fluoridation and oxidation in HF solution rather than the two views proposed in Figure 4.

This synergetic mechanism of fluoridation and oxidation was also found in Ni–Cr–Mo alloy, Ni–Cr–Fe alloy and Ni–Cu alloy (Dai et al. 2020b). It is worth noting that the passivation was driven by various elements, thus leading to different types of passive film formed on surface to protect the matrix from further corrosion. For Ni–Cr–Mo alloys, the surface passive film mainly consisted of Mo-rich substances (Mo oxides and its hydrates) (Li et al. 2015). While in terms of Ni–Cr–Fe alloys, the oxides, fluorides and hydrates of Ni, Cr, and Fe were detected in passive film, and their thermal stability were higher than Mo oxides and its hydrates (Dai et al. 2020b). For Ni–Cu alloys, Cu matrix, oxides and fluorides with lowest degradation performance and free defects were formed in order to prevent the severe attack of HF solution (Crook et al. 2007; Rebak et al. 2001; Yang et al. 2020a,b). Compared with other two alloys, Ni–Cu alloys showed the highest corrosion resistance due to the best performance of passive film (Braun et al. 1957; Copson and Cheng 1956; Crum et al. 1999; Jennings 2010; Kumar and Chatterjee 2005; Yu et al. 2015). The corresponding schematic illustrations are shown in Figure 5.

Although the corrosion behavior of Ni–Cr–Mo alloys, Ni–Cr–Fe alloys and Ni–Cu alloys in HF solution can be well explained by Figure 5, the premise is that the microstructures of these alloys are homogeneous. Considering that inclusions and intermetallic precipitation phases are impossible to avoid, the corrosion mechanism in HF solution is inevitably impacted by these substances. The additional local galvanic effect caused by these substances would promote the degradation of material, which mainly resulted from the destruction of the surface passive film by local corrosion (Dai et al. 2020b). Therefore, when the microstructure of nickel-based alloys is inhomogeneous, the corrosion mechanism needs to be reconsidered.

3.3 Ti and Ti alloys

Titanium and titanium alloys were mainly used for denture implantation and nuclear spent fuel treatment equipment (Hofmann and Sanz 1982; Milošev et al. 2013; Souza et al. 2012). The premise of safe operation of Ti alloys relied on the nanothick passive layer (oxides) formed on surface (Souza et al. 2015) through a reaction in Eq. (2). These compact substances adhered on surface could mitigate the invasion of medium to matrix (El-Mahdy et al. 1996; Fojt et al. 2015). In these applications, fluoride ion existed in the form of fluoride salt, but it was also doped with some other acid medium (e.g. CH_3COOH , $\text{C}_3\text{H}_6\text{O}_3$, $\text{C}_6\text{H}_8\text{O}_7$ and HCl), which made fluoride ion reacted with these acids to generate HF. As a result, Ti alloys were also confronted with the corrosion threat by HF. The passive film formed on Ti and its alloys suffered severe attack from fluoride ion and was gradually degraded (the degradation nature is to form soluble fluoride on passive film). But this only

Figure 5: Corrosion mechanisms of Ni–Cr–Mo alloys, Ni–Cr–Fe alloys and Ni–Cu alloys in HF solution. Adapted from Ref (Dai et al. 2020b; copyright 2020, with permission from Elsevier).

occurred when the concentration of fluoride ion in solution reached a critical value (Li et al. 2001, 2007; Wilhelmsen and Grande 1987). As reactions shown in Eqs. (5)–(10) (Golvano et al. 2015), the degradation mechanism of passive film was similar to the fluoride ion induced passive film degradation process in Section 3.1. The difference was that the attack of fluoride ion to Ti alloys was only limited to the subsurface (on nanoscale), which was attributed to the strong repassivation ability of Ti alloys (Wang et al. 2016). The degradation of passive film could be described by Eq. (11). When fluoride ion concentration was higher (Wang et al. 2014; Wilhelmsen and Grande 1987), Na_2TiF_6 was formed by the dissolution of passive film TiO_2 , which had no protection for the matrix although it was more stable than TiO_2 (Huang 2002). Once the passive film had a weak area (such as defects), fluoride ion was easier to attach and destroy the passive film, resulting in the formation of metastable pits (Reclaru and Meyer 1998; Strehblow et al. 1979; Wang et al. 2016; Wilhelmsen and Grande 1987). For some Ti alloys with poor passive film, metastable pits were likely to develop to open pits (Schiff et al. 2002; Wang et al. 2014, 2018).

4 Influencing factors for corrosion in HF solution

4.1 Chemical composition

The chemical composition of materials is one controlling factor in its passivation process. Different elements not

only lead to various passivation mechanisms, but also determine the stability of the passive film and affect the corrosion resistance in HF solution. At present, the influences of chemical elements were mostly studied for nickel-based alloys.

4.1.1 Mo

Compared with other elements (e.g. Cr, Fe, and Cu), Mo element was beneficial in HF corrosion process, which dominated the formation of passivation process (Yang et al. 2019). From the view of atomic structure, the atomic number of Mo element was large with five layers of electron, and the atomic nucleus had a weaker binding force on the outmost layer electrons (Zolotov 2007). As a result, the electron loss ability of Mo element was much higher than that of Cr, Fe, and Ni elements, and the reducibility order of these elements was $\text{Mo} > \text{Cr} > \text{Fe} > \text{Ni}$ (Lide 2004). Therefore, when Mo-containing nickel-based alloys were attacked by HF solution, Mo element would preferential participate in the passivation process due to its strong reducibility and form a layer of Mo-rich passive film (Dai et al. 2020b). This layer of Mo-rich substance effectively slowed down further intrusion of the medium into the matrix (Moon et al. 2019; Santos et al. 2020). Li et al. (2015) characterized the chemical composition of NiCoCrMo alloy surface after corrosion in 5.2 M HF solution, intense Mo spectrum peak was detected, and the Mo content was up to 50 atomic % in the outmost layer of passive film. In addition, some scholars (Hou et al. 2014; Li et al. 2014; Zhang et al. 2014a,b) conducted more detailed analysis on the chemical composition of Mo-containing nickel-based alloys and

found that the content of Co, Fe, and Cr in these original alloys was not lower than that of Mo element, but the former substances were not significantly detected in surface products after corrosion. In addition to the easy passivation of Mo, due to its strong reducibility, Dai et al. (2020b) considered that Mo could inhibit or slow down other low-reducing elements from participating in the reaction when suffered from HF attack.

Moreover, Mo-rich passive film is the main barrier against corrosion attack, whose properties directly affect the corrosion behavior and lead to different corrosion resistances. The content of Mo is the key factor affecting the performance of the surface Mo-rich passive film (Mosayebi et al. 2020). Hou et al. (2015a,b) found that the weight loss of NiCoCrMo alloy reduced by 44% with Mo content increasing from 7 to 15 wt%, which was ascribed to improved performance of Mo-rich passive film. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) proved that Mo content in corroded solution also gradual decreased, which meant that the passive film of alloys with 15 wt% Mo was the best with the lowest degradation (Yang et al. 2020a,b). However, there seems to be a threshold value for Mo content, which can be seen from the corrosion rates of nickel-based alloys containing various Mo content. In Figure 6a, the corrosion rate of nickel-based alloys significantly increased with Mo content increasing from 8.1 to 16 wt% in various concentrations of HF solution (1–30%). The corrosion rate slightly increased when Mo content increased from 16 to 17 wt%, which was similar to results in Figure 6b. One thing to be noted was that the corrosion resistance of Haynes 242 with 25 wt% Mo was higher than Hastelloy C-22HS annealed with 17 wt% Mo in

Figure 6: (a) The corrosion rates of various nickel-based alloys containing Mo in different concentrations of HF solution at 52 °C for 240 h, which were taken from Crook et al. (2007). (b) Corrosion rate of some nickel-based alloys containing Mo after corrosion in 20 wt% HF solution at 79 °C for 240 h, including high Mo content alloys, which was obtained from Rebak et al. (2001; copyright 2001, with permission from Wiley).

Figure 6b, while the corrosion resistance of alloys with 28.5 wt% Mo decreased. So, it seems that the relationship between Mo content and corrosion rate is not linear. That is, Mo content is not always protective for alloys in HF solution. When Mo content exceeds a threshold value, the corrosion resistance will be reduced rather than increased again. Mosayebi et al. (2020) evaluated the effects of Mo content on the structure and corrosion behavior of Ni–Mo electroplated coatings in chloride mediums. They found that when the Mo content of coating exceeded 15 wt%, the structure of Mo-rich passive film became worse, and a large number of cracks formed and seriously damaged its protective function. It suggested that excessive Mo affected the quality of Mo-rich passive film on the surface. However, the underlying reason for the above phenomenon is still not well understood.

4.1.2 Cr and Fe

For alloys without Mo element, due to the similar atomic structure of Fe and Cr elements, the reducibility difference between these two elements is not large. So in HF solution, these two elements participate in passivation at the same time and hinder corrosion. For Ni–Cr–Fe alloys in HF solution, a strong Cr 2p peak and Fe 3p peak was detected in surface passive film, including large amount of Cr_2O_3 , $\text{Cr}(\text{OH})_3$, Fe_2O_3 and small part of CrF_3 and FeF_3 (Dai et al. 2020b). Similarly, Fe_2O_3 and Cr_2O_3 were also found in the passive film of Fe–Cr–Ni austenitic SS (Zou et al. 2018). Dai et al. (2020b) calculated the standard Gibbs free energy of formation of these substance and Mo compounds using HSC 6.0, and found that compared to Mo compounds, the standard Gibbs free energy of formation of Fe and Cr oxides, fluorides, and hydrates was more negative. It suggested that the latter showed higher thermal stability and could resist severe attack by HF. Besides, the beneficial effects of Cr and Fe were reported in molten fluoride-salt corrosion (Chan et al. 2018; Liu et al. 2020a,b; Pavlik et al. 2015) and the oxidation of primary water (Langelier et al. 2016; Lozano-Perez et al. 2009; Volpe et al. 2019). When suffered medium attack, Cr_2O_3 could quickly formed and acted as an effective barrier to prevent further permeation of O^{2-} (Kuang et al. 2017), thus improving corrosion resistance. From the corrosion rates of Ni–Cr–Fe alloys (Inconel 600) and Ni–Cr–Mo alloys (Hastelloy C-276, Hastelloy B3 and Haynes 242, etc.) in HF solution (Pawel 1994), it was found that the former ones showed higher corrosion resistance than the latter, which was ascribed to the formation of more beneficial Fe and Cr compounds in passive film.

4.1.3 Cu

The less active copper element was often used as an alloy additive element, which aimed to improve the corrosion resistance of materials (Inouye et al. 1976; Jang et al. 2009a,b). Many studies had explored the effect of Cu on the corrosion performance of alloys in HF solution (Braun et al. 1957; Copson and Cheng 1956; Hou et al. 2015a,b; Jennings 2010; Kumar and Chatterjee 2005; Li et al. 2015; Yang et al. 2017, 2020a,b; Zhang et al. 2014a,b). In HF solution, Cu not only slowed down substance exchange between metal and the medium at the initial stage, but also reduced the degradation of passive film at later stage. From the perspective of electrochemical corrosion, Cu was a special element that the standard electrode potential of Cu/Cu^{2+} was the highest (0.337 V (Lide 2004)) compared with other elements (Figure 7). The highest standard electrode potential of Cu resulted in the lowest reaction activity of alloy containing Cu, so that these alloys were more stable in HF solution. Yang et al. (2020a,b) found that the addition of 2 wt% Cu into Ni–Co–Cr–Mo alloy could significant improve its corrosion resistance in HF solution by changing the nature of passive film and accelerating the formation of Cu-rich passive film instead of Mo-rich film. In addition, they also pointed out that Cu dominated passive film prevented the severe attack by HF at weak area (e.g. grain boundary) in contrast to Mo-rich passive film (Yang et al. 2020a,b). The excellent Cu-rich passive film was found to be composed of Cu matrix, oxides and fluorides with free defects and higher stability, making it predominant in surface film (Hao et al. 2017; Hayashi et al. 2020; Li et al. 2015). Compared with other metallic passive films, the degradation of Cu matrix, oxides and fluorides was lower (Liu et al. 2020a,b; Yang et al. 2020a,b; Zhang et al. 2014a,b), suggesting that Cu passive film retarded corrosion and damage imposed by HF solution.

Figure 7: The standard electrode potential of various elements, this graph was drawn based on the data from the research of (Lide 2004).

4.2 Environmental factors

4.2.1 Oxygen

Metallic materials exhibited distinct corrosion resistance in HF solutions with aeration (air) and nitrogen. The corrosion rate of Monel 400 in 25% HF solution at 30 °C saturated with air was approximately two orders of magnitude higher than purged with N₂ (Schillmoller 1993). Schillmoller (1993) observed that an adherent brown fluoride film formed on Monel 400 in nitrogen purged environment, in contrast to a loose and nonadherent film in aerated condition. It was suggested that air or oxygen in aqueous acid solutions accelerated corrosion by promoting the formation of useless product layer. In other corrosive medium, compared with solution without oxygen, solutions containing trace dissolved oxygen (<10 ppm) was proved to make the material in a reductive state of active dissolution (Gong et al. 2020; Xue et al. 2018), thus accelerating degradation. Moreover, the effect of oxygen content was also investigated. Figure 8 shows the corrosion rates of Monel 400 and some alloys with high content of Cu in HF solution. The corrosion rates of Monel 400, 70/30(Cu/Ni), and 90/10(Cu/Ni) slightly increased with 500 ppm oxygen, while increased substantially with more than 1500 ppm oxygen (Schillmoller 1993). The corrosion rates of Monel 400, 70/30(Cu/Ni), and 90/10(Cu/Ni) firstly increased and then slightly decreased with increasing oxygen concentration in 38% HF solution, with the threshold value of dissolved oxygen content of 4700 ppm (Figure 8). Excessive dissolved oxygen will not cause more degradation. Although the presence of dissolved oxygen promoted anodic dissolution process, the accumulation of surface products intensified with the continuous increase of oxygen content (Aguirre et al. 2019; Kuang et al. 2013). When oxygen content reached a certain critical value, the thickness of product layer was sufficiently high that it acted as an obstacle to slow down the diffusion rate of the medium into the matrix (Xue et al. 2018). However, the growth of corrosion products was always accompanied by the formation of defects (Shen et al. 2019; Zhang et al. 2018), which resulted in less significant decrease in corrosion resistance due to the higher defect density in HF solution with high dissolved oxygen content.

4.2.2 HF concentrations and temperature

NACE 5A171-2007 recommended material selection (carbon steels, stainless steels and nickel-based alloys, etc.) for various concentrations of HF solution and temperatures

based on corrosion rate below 0.51 mm/y. Almost all materials could stay stable in high concentration HF solution (>70 wt%), which was attributed to the formation of a dense and highly adhesive fluoride layer on the surface, thus effectively preventing further corrosion (Schillmoller 1998a,b; Schmitt et al. 2004; Schussler 1955; van der Merwe 2016; van der Merwe et al. 2016). Austenitic SS (316L, 904L, 2205) could retard the invasion of fluoride ion due to the formation of some beneficial oxides as a result of the addition of several noble elements (e.g. Cr, Ni, and Mo). While at medium concentration of HF solution, the benefits brought by these elements lost and only nickel-based alloys and some high-Cu alloys could meet the requirement for corrosion resistance (Kumar and Chatterjee 2005; Misener et al. 1985; Penuela and Chirinos 1999; Tyreman 1986). HF solution with low and medium concentration was highly corrosive, and the extent of uniform thinning increased with increasing concentration, which might be ascribed to more free fluoride ion in solution due to the large ionization degree of HF (Chen et al. 2020a,b). The structure of product formed in low and medium concentration HF solution was not as good as in high concentration (Dai et al. 2020a). For some nickel-based alloys, such as Monel 400 and Hastelloy series alloys, internal attack was found in HF solution. As the concentration of HF increased (at medium and low concentrations); the internal penetration depth of these alloys was accelerated in both vapor and liquid phases (Rebak et al. 2001). So, it seems that the effect of HF concentration is not to change the internal attack mode of HF, but to aggravate the degree of internal attack.

Figure 8: The corrosion rates of Ni-Cu alloys as a function of oxygen content in HF solution. This graph was drawn based on the results reported in Schillmoller (1993).

With increasing temperature, the ionization of HF ($\text{HF} \leftrightarrow \text{H}^+ + \text{F}^-$, $\Delta H > 0$) was promoted, and the diffusion rate of medium in solution also increased. According to Arrhenius formula, within a certain range of temperature, there was a positive linear relationship between $\ln K$ and $1/T$, which meant that the increase in temperature promoted chemical reaction rate between metal and medium. Thus, the material was more vulnerable to corrosion at high temperature (Pawel 1994). The increase in temperature promoted the dissolution of the passive film, and its protective properties gradually lost (Crook et al. 2007). Therefore, in HF at high temperatures, some nickel-based alloys with excellent corrosion resistance were selected instead of stainless steels and carbon steels. Although Monel 400 was subjected to intergranular attack by HF vapor, the temperature did not significantly affect the internal attack degree. In contrast, the corrosion of Hastelloy C-2000 in HF solution or vapor environment was sensitive to temperature, and severe attack would be activated at certain temperature (Osborne 2002; Rebak et al. 2001). Therefore, for some alloys, temperature tended to change the attack mode of HF. Namely, internal penetration was activated, and uniform corrosion changed to internal attack.

4.2.3 Phase state

HF is prone to volatilize even at room temperature. A HF vapor environment was easily formed during service condition, and the corrosion damage by HF vapor should also be paid attention (Whitaker 1950). The corrosion properties of metallic materials in liquid phase and vapor phase of HF were different. Pawel (1994) lists corrosion rates of various metallic materials (including SSs and nickel-based alloys) in different HF environments. For 316L SS, its corrosion rate in HF vapor was lower than in liquid phase. Similar trend was also found in carbon steels (Jennings 2001), which was attributed to the formation of compact fluorides with excellent protection on surface in vapor environment (Hashim and Valerioti 1993; van der Merwe 2016; van der Merwe et al. 2020). It should be noted that a large amount of fluorides was also detected in surface product of carbon steels (Dai et al. 2020a) and SSs (Chen et al. 2020a,b; Jiang et al. 2019; Zou et al. 2018) after immersion in HF solution, but this substance was less protective for the matrix. It suggested that the structure and performance of surface products in liquid and vapor phase of HF are different. Even if the same substance is generated, due to the difference in microstructure, these substances will show different protective contributions.

By contrast, nickel-based alloys (C-22, C-276, Ni200, 825, 400, 600, and 20) showed the opposite trend, which suffered more severe attack in HF vapor, especially at high concentration of HF and high temperature (Osborne 2002; Pawel 1994). The internal attack mode in HF is different and depends on the phase state of HF. In long-term corrosion, Monel 400 and other alloys containing Cu (Braun et al. 1957; Holmberg and Prange 1945; Pray et al. 1953) showed severe IGC in HF vapor and higher corrosion rate, in contrast to uniform corrosion in HF solution (as shown in Figure 9). Similarly, Hastelloy C-2000 and Inconel 600 also suffered intense attack by HF vapor, while the discrepancy in damage degree between HF vapor and HF solution was different for various alloys (Figure 9), which might be ascribed to alloying elements.

4.2.4 Mixed with other ions

The incorporation of other acid ions (such as Cl^- and SO_4^{2-}) were often an important problem for HF or fluoride ion corrosion (Heakal et al. 2011; Wang et al. 2015a,b). The corrosion behavior of material in these environments was affected by the interaction between ions (including competitive adsorption, corrosion promotion, etc.). Table 3 is a summary of the effect of fluoride ion in mixture solutions. It is known that spontaneous passivation occurred in other acidic environment, and a compact passive film was formed to prevent corrosion. However, fluoride ion always threatened the passive film, which promoted the

Figure 9: Corrosion rate calculated by weight loss of engineering alloys in wet HF (Rebak et al. 2001), “L” indicates that sample is immersed in HF solution (liquid phase) and “V” indicates that sample is suspended above the liquid level of HF solution (vapor phase). (Copyright 2001; with permission from Wiley).

Table 3: Summary of the effect of fluoride ion in mixed solutions.

Material	Medium	Test	Characterization method	The effect of fluoride ion	References
F ⁻ and Cl ⁻					
Pure Ti	Artificial saliva solution with 0.02–2% NaF (pH = 7.0 and 4.0)	Immersion test and electrochemical test	Inductively coupled plasma mass spectroscopy (ICP-MS), ion meter with fluoride ion	A ₁ fluoride ion accelerated the dissolution of passive film, especial in pH = 4.0	Nakagawa et al. (1999)
Ti-0.15%Pd	1 M NaCl with 1 M NaF	Electrochemical test	SEM	A ₁ pit corrosion induced by Cl ⁻ is inhibited by fluoride ion by mean of controlling the anodic polarization process	Brossia and Cragolino (2001)
Ti grade 2 and Ti grade 7	1 M NaCl with 0–0.1 M NaF	Electrochemical test	SEM	A ₁ fluoride ion altered the dissolution kinetic of Ti alloys, thus improving the current density with increasing fluoride ion concentration	Brossia and Cragolino (2004)
Pure Ti	Hanks' balanced salt solution with 0.04–0.4 ppm NaF (pH = 7.3 and 5.0)	Immersion test and electrochemical test	SEM, XPS, (inductively coupled plasma atomic emission spectrometry) ICP-AES	A ₁ the TiO ₂ passive film dissolved when suffered fluoride ion attack	Chen et al. (2020a,b)
Pure Ti	1% NaCl + 0–1% NaF (pH = 6)	Electrochemical test	SEM and XPS	A ₁ fluoride ion penetrated into passive film, thus leading to reduced protection	Huang (2002)
Pure Ti and Ti alloys	0.9% NaCl + 0.2% NaF (pH = 3.8)	Discoloration test	SEM and ICP-OES	A ₁ fluoride ion induced higher dissolution degree of material	Noguchi et al. (2008)
Pure Ti	Artificial saliva solution with 0–900 ppm NaF addition (pH = 4.2 or 6.5)	Electrochemical test	ICP-MS	A ₁ fluoride ion induced titanium corrosion in acidic environment, while the effect of fluoride ion is not prominent in neutral environment	Fukushima et al. (2018)
Ti alloys (TiAl6V4)	Fusayama Meyer artificial saliva with 1000 ppm fluoride ion	Electrochemical test	SEM	A ₁ fluoride ion caused the breakdown of passive film and even pit corrosion.	Schiff et al. (2002)
Pure Ti	9 g/L NaCl with (1, 2.5) g/mL NaF (pH = 4.0 and 7)	Electrochemical test	–	A ₁ in acidic environment, the resistance of passive film was greatly reduced by fluoride ion attack, which was only relatively stable in neutral solution	Boere (1995)
Pure Ti, Ti alloys and 316L SS	1. Artificial saliva with 0.1% (KF and NaF) 2. 1% NaCl + 0.1% KF (pH = 6.15–3.0)	Electrochemical test	SEM and EDS	A ₁ fluoride ion was prone to aggress the protective passive film of Ti and its alloys, and may cause local corrosion	Reclaru and Meyer (1998)
Pure Ti	In artificial saliva with 20–277 ppm F ⁻ (pH = 5.5), 12300 ppm F ⁻ (pH = 6.5)	Electrochemical test and wear test	SEM	A ₁ a significant degradation of passive film can be found in high concentration of fluoride ion	Souza et al. (2012)
Pure Ti and Ti6Al4V	Fusayama's artificial saliva solution with 20–277 ppm F ⁻ (pH = 5.5), 12300 ppm F ⁻ (pH = 6.5)	Electrochemical test	SEM, EDS, AFM, XPS, and ICP-MS	A ₁ fluoride ion promoted the transition from compact film to porous film; in high fluoride ion solution, pure Ti was degraded by pit corrosion and while Ti6Al4V suffered general corrosion with microcrack	Souza et al. (2015)
2205 duplex SS (DSS) and 316L SS	In artificial saliva with 1000 ppm NaF (pH = 5.3)	Electrochemical test	XPS	A ₁ the addition of fluoride ion slightly decreased the passive range of two materials, the resistance of 2205 DSS was higher than 316L SS	Kocijan et al. (2011)

Table 3: (continued)

Material	Medium	Test	Characterization method	The effect of fluoride ion	References
Aluminium	0.5 M Cl ⁻ with 0.25×10^{-3} –0.25 M F ⁻	Electrochemical test	–	A, fluoride ion modified surface oxide into a complex oxy-fluoride film in such a way as to facilitate attack by chloride.	Carroll et al. (1993)
Pure Ti and Ti6Al4V	Ringer's solution with 10 g/L F ⁻ (pH = 5.5)	Electrochemical test	OM	A, severe attack on these alloys was induced by fluoride ion in acidic environment	Toumelin-Chemla et al. (1996)
Super-austenitic stainless steels	0.084–0.42 M NaCl with 0.79 M KF (pH = 3)	Immersion test and electrochemical test	–	Uncertainly, the passivation region of two SSs was narrow in fluoride ion containing solution	Bastidas et al. (1996)
403 martensitic stainless steel	0.1 M NaCl + 1 M NaF and 0.5 M HF + 0.5 M HCl	Immersion test	–	A, the fluoride ion increases the pitting corrosion potential of material in Cl ⁻ bearing solution, and the passive current density also enhanced	Pahlavan et al. (2016)
316 SS	0.01 M HCl + 0–0.1 M NaF	Electrochemical test	XPS	A, the addition of fluoride ion reduced the passivation resistance at high concentration, low concentration of NaF had no influence on passivation performance of 316 SS (the aim of fluoride ion was to dissolve the oxides film)	Li et al. (2001)
Ti-5Nb-7Zr-5Ta, pure Ti and Ti6Al4V	Artificial saliva with 1500 ppm NaF (pH = 5.5)	Immersion test	SEM and EDS	A, fluoride ion increased surface roughness by attacking passive film	Miotto et al. (2016)
Ti-10Nb-10Zr-5Ta F ⁻ and SO ₄ ²⁻	Artificial saliva with 1000 ppm NaF (pH = 2–7)	Electrochemical test	XRD	A, higher degradation was found in fluoride ion-rich acidic saliva (pH = 2)	Braic et al. (2015)
400, 430 and 304 SS	0.01 M H ₂ SO ₄ with 0–1.0 M KF	Immersion test and electrochemical test	SEM and XPS	A and R, 0.01 M fluoride ion was added in 0.01M H ₂ SO ₄ to shorten passivation of SSs, while the passive film resistance of SSs was improved with increasing fluoride ion concentration, which was attributed to the hydration of fluoride ion (increasing pH) in solution	Sekine et al. (1994)
Pure Ti	1 M H ₂ SO ₄ with 0–0.12 M NaF	Electrochemical test	–	A, fluoride ion accelerated active corrosion and resulted in more active, time-dependent corrosion potentials and greatly increased current requirements for passivation	Mandry and Rosenblatt (1972)
Pure Ti and Ti alloys	0–0.003 M NaF (pH = 1.0 which is controlled by 98% H ₂ SO ₄)	Electrochemical test	XPS	A, fluoride ion permeation in passive film increased with fluoride ion concentration, Ti alloys showed better corrosion resistance than pure Ti, which was related to the beneficial effect by noble elements (Pd, Mo, and Ni)	Wang et al. (2016)
Ti	0.45 M H ₂ SO ₄ with 1.0×10^{-2} – 2.5×10^{-1} M NaF	Electrochemical test	SEM, TEM and secondary ion mass spectrometry (SIMS).	A, fluoride ion accelerated the dissolution of TiO ₂ passive film from the outmost to inside	Kelly (1979)
Pure Ti	0.05 M H ₂ SO ₄ with 0–0.005 M NaF (pH = 1)	Electrochemical test	XPS	A, 0–0.0005 M fluoride ion addition made passive film unstable; exceeded 0.0005 M fluoride ion, the passive film is remarkable dissolved	Wang et al. (2014)
Pure Ti	0.05M SO ₄ ²⁻ with 0–0.05 M NaF (pH = 1–5)	Electrochemical test	XPS	A, when fluoride ion concentration exceeded a critical value, the passive film dissolved. A quality relationship between the concentration of fluoride ion and pH was established ($\partial pF / \partial pH = 0.17$ (pH = 1.0–2.5), $\partial pF / \partial pH = -0.78$ (pH = 3.0–5.0))	Wang et al. (2015a,b)

Table 3: (continued)

Material	Medium	Test	Characterization method	The effect of fluoride ion	References
Pure Ti and 316 SS	0.05 M H_2SO_4 , 0–5 mM NaF	Electrochemical test	SEM and XPS	A, fluoride ion changed passive film by accelerating anodic process	Wang et al. (2018)
304 SS, 2507 DSS and 904L SS	89% H_2SO_4 with 6% NaF	Electrochemical test	SEM and EDS	R, the addition of fluoride ion induced more stable NiF_2 instead of NiS , thus protecting matrix more efficiently	Yu et al. (2017)

“A” represents the fluoride ion contributed to accelerate the corrosion process. “R” refers to the fluoride ion prone to retard the corrosion process. There is Cl^- exists in artificial saliva solution.

transformation of a compact passive film to a porous product film, reducing the protection role of the passive film.

In Cl^- containing environment (Boere 1995; Burstein and Souto 1995; Houb-Dine et al. 2018; Souza et al. 2012), the addition of fluoride ion would change corrosion process. For pure Ti and Ti alloys, the fluoride ion followed the reaction of Eqs. (5)–(11) to transform TiO_2 passive film into soluble TiF_6^{2-} (Nakagawa et al. 1999). While for austenitic SSs, Cr_2O_3 -dominated passive film became semisoluble CrF_3 when suffered from severe attack by fluoride ion (Kocijan et al. 2011; Trompette 2015). The weakening effect of fluoride was more prominent in Ti alloys, which was mainly due to the formation of a large number of soluble substances (Stancheva and Bojinov 2012). It was interesting to note that Cl^- in these mixed solutions showed no pitting, which was attributed to the competition adsorption with fluoride ion (Soltis 2015). According to the relationship of Jones–Dole (Jenkins and Marcus 1995), Cl^- was regarded as chaotropes (water structure destroyer) with negative coefficient B (which referred to the attachment strength of surrounding water molecule to ions), while F^- worked as kosmotropes (water structure maker) with positive B (Collins et al. 2007; Marcus 1991; Trompette 2014). As a chaotropes, Cl^- could quickly get rid of surrounding water molecules to attack local weaken area of passive film (Ningshen et al. 2007) by replacing oxygen ions. In contrast, fluoride ion was tightly surrounded by water molecules, so fluoride ion was more prone to evenly accumulated on the passive film first followed by uniform degradation (Trompette 2014). The opposite hydrate property of fluoride ion affected the formation of pits induced by Cl^- . For Ti alloys, Cl^- induced pit by occupied the position of oxygen ions in passive film, when fluoride ion dissolved the passive film uniformly, the incorporation of Cl^- was blocked by fluoride ion, thus pit could not grow (Wang et al. 2018). On the other hand, the increase of pitting initiation potential of 403 martensitic stainless steel (Pahlavan et al. 2016) was also reported, which was related to the weak acid nature of HF (Kappes 2020). Although the nucleation of metastable pits was accelerated by fluoride ion in Cl^- bearing solution, fluoride ion inhibited pit growth based on Galvele’s localized acidification theory (Galvele 1976). The weak electrolyte nature of HF resulted in incomplete ionization of F^- and H^+ , so the pH value at the bottom of pit was relatively high which was unfavorable for the growth of pits (Pahlavan et al. 2016). Similarly, Carranza et al. (2007) and other scholars (Day and Rebak 2004; Rebak 2005a,b) concluded that fluoride behaved as an inhibitor of chloride-induced crevice corrosion of Alloy 22 from the same perspective. However, the presence of Cl^- in solution is favorable for fluoride ion attack. For austenitic

SS, Cl^- incorporation into passive film occupied the position of oxygen ions until Cr oxides and hydroxide were dissolved into soluble Cr^{3+} by catalyzing process (Soltis 2015; Wang et al. 2013; Wegelius et al. 1999). The large number of Cr^{3+} generated by the catalytic mechanism of Cl^- provided more reactants for F^- to produce semisoluble CrF_3 . Thus, the corrosion process or the degradation process of fluoride ion was accelerated by Cl^- (Wang et al. 2018).

In addition, an acceleration effect was also found in F^- and SO_4^{2-} mixture solution (Kelly 1979; Mandry and Rosenblatt 1972; Sekine et al. 1994; Wang et al. 2016). Numerous studies concluded that this phenomenon was due to the active dissolution of fluoride ion (Wang et al. 2015a,b). In dilute sulfuric acid environment, the addition of fluoride ion changed the passivation process and transformed it into an activation-passivation behavior by attacking passive film (Wang et al. 2018). The formation of unstable passive film due to the attack of fluoride ion in F^- and SO_4^{2-} mixture solution greatly reduced the corrosion resistance. While in a concentrated sulfuric acid environment with fluoride ion, the corrosion resistance of 304 SS, 904L SS and 2507 duplex phase SS were increased, which was attributed to the preferential affinity of fluoride ion (Yu et al. 2017). It was proved that the concentrated sulfuric acid made the material in a state of activation to passivation (Li et al. 2006), and the state directly changed to passivation after the addition of fluoride ion, which was due to the fact that the less protective NiS was replaced by more compact NiF_2 . The stability of NiF_2 was excellent so that the matrix was better protected (Yu et al. 2017).

Moreover, pH is also a key factor affecting the performance of the dissolution ability of fluoride ion in mixture ions system. Fovet et al. (2001) noted that the dissolution of TiO_2 passive film could be avoided by controlling pH within certain range in fluoride ion-containing solution. Acidic environment was favorable for stimulating the activity of fluoride ion, thus the dissolution rate of TiO_2 was accelerated (Nakagawa et al. 1999), while, the stability of passive film could be ensured in alkaline environment (Braic et al. 2015). A quantitative relationship was established between fluoride ion concentration and pH value in mixture ions system, and it was beneficial for the control of pH range to know the critical fluoride ion concentration to avoid significant degradation (Wang et al. 2015a,b).

4.3 Stress

The introduction of stress remarkable accelerated corrosion process and equipment failure. Stress could be

roughly divided into four types: working stress, residual stress, thermal stress, and structural stress (Rebak 2005a,b; Turnbull 1993). These stresses may be static, variable, internal, or external, which will lead to stress corrosion cracking (SCC) and corrosion fatigue (CF) when immersed in corrosive media. The internal damage mechanisms of SCC and CF were ascribed to the coupling between mechanical and chemical stressors (Masoumi et al. 2019; Zhou et al. 2017), which was more complex than general corrosion process.

SCC of metal and alloys were prone to occur in HF solution, especially for conditions where material showed higher corrosion sensitivity. Table 4 shows the SCC information of nickel-based alloys using U-bend specimens. The stress corrosion sensitivity of alloys can be evaluated by its internal attack in general corrosion. Alloys suffered high corrosion damage and severe internal attack by HF would preferentially crack (Crook et al. 2007; Rebak et al. 2001; Schillmoller 1993), which was based on the theory of anodic dissolution. It was reported that the SCC of Monel and other high nickel-based alloys in HF environment was related to its heat treatment, stress, time and exposed condition (Copson and Cheng 1956). The stress release heat treatment process could slow down the probability of SCC of Monel alloys (Copson and Cheng 1956). In addition, Schussler (1955) reported that completely immersing Monel 400 and alloys containing Cu in HF solution effectively prevented the initiation of stress corrosion cracks, which was due to the fact that alloys had low corrosion rate. Besides, the SCC of other nickel-based alloys in HF solution or vapor environment was also investigated (Pawel 1994), but with the emphasis on cracking time and crack length, while the internal cracking mechanism was merely mentioned. For carbon steels, Dai et al. (2020a) proposed a SCC mechanism for Q345R in HF solution (Figure 10), which was based on the mechanism of pits induced crack, and they found that tensile stress not only shortened the time for pit initiation and growth, but also accelerated pit-to-crack transition. In terms of hydrogen embrittlement mechanism, Warren (1987) found hydrogen blistering in carbon steel in AHF and HF solution, and it developed for carbon steel with more inclusions containing oxide and sulfide content, which was ascribed to inclusion defects acting as hydrogen trap to capture hydrogen (Merrick 1989). Jennings (2001) reported failure cases of hydrogen-assisted stress corrosion cracking of carbon steels and low alloy steel fasteners in HF solution or AHF, which was due to the hydrogen embrittlement failure mechanism caused by the adsorption of large amounts of hydrogen by deformed martensitic. For pure Ti, a stress corrosion embrittlement cracking mechanism based on

Table 4: Stress corrosion cracking of nickel-based alloys using U-bend specimens (Rebak et al. 2001; copyright 2001, with permission from Wiley).

Alloys	U-bend specimens in 20% HF, 240 h	Average general corrosion rate (mm/y)	Average crack or preferential penetration rate, 10^{-11} m/s	Observations (physics appearance of sample's surface after corrosion and its corrosion form)
Monel 400	66 °C, L	0.165	1.5	Shiny original metallic. Shallow IGA.
	66 °C, V	6.48	160	Black. Severe IGA, fissures
	79 °C, L	0.003	1.5	Intense Cu color. 0.05 mm thick layer of Cu on surface
	79 °C, V	6.78	15	IGA
	93 °C, L	0.003	1.5	Cu color. Crystalline lumps of Cu on the surface
	93 °C, V	3.81	1.5	Ni plated appearance. Shallow IGA
Hastelloy C-276	66 °C, L	2.95	1.5	Ni plated appearance. Uniform corrosion.
	66 °C, V	1.08	1.5	Small corrosion pits. Green corrosion product ($\text{NiCrF}_5 \cdot 7\text{H}_2\text{O}$)
	79 °C, L	6.07	1.2	Dark gray sample. Uneven general corrosion, especially in stressed areas crevice corrosion
	79 °C, V	2.39	3.0	Light gray sample. Uneven penetration. Small corrosion pits. Green corrosion product ($\text{NiCrF}_5 \cdot 7\text{H}_2\text{O}$)
	93 °C, L	0.732	68	Ni plated appearance. SCC, pitting, and crevice corrosion. Black corrosion products in creviced area. Compressive side attack.
	93 °C, V	0.798	24	Ni plated appearance. SCC. Green corrosion product ($\text{NiCrF}_5 \cdot 7\text{H}_2\text{O}$)
Hastelloy C-2000	66 °C, L	0.856	1.5	Dark gray color. Shallow sponge like surface appearance
	66 °C, V	0.864	1.5	Ni plated appearance. Uniform corrosion. Green corrosion product ($\text{NiCrF}_5 \cdot 7\text{H}_2\text{O}$)
	79 °C, L	0.411	13	Light Cu color. Small crevice corrosion. Thin band of forest-like penetration
	79 °C, V	0.363	5.9	Bluish color with dotted areas of Cu color. Small crevice corrosion. Thin hair-like penetration
	93 °C, L	0.353	32	SCC. On compressive side, cracks paralleled to surface
	93 °C, V	0.376	1.5	Ni plated appearance. Small crevice corrosion. <1 μm Cu granules on surface
Haynes 242	66 °C, L	1.82	1.5	Light gray color. Sponge like surface (metal flaking). Crevice corrosion
	66 °C, V	0.683	2.0	Sponge like appearance. Uneven corrosion in stressed areas
	79 °C, L	1.66	13	Dark gray color. Uneven sponge-like corrosion in stressed areas. Small crevice corrosion. Pitting
	79 °C, V	0.503	3.5	Bluish color. Small crevice corrosion. SCC.
	93 °C, L	0.434	43	Dark gray color. SCC, pitting, and crevice corrosion
	93 °C, V	0.615	16	Ni plated appearance. Shallow crevice and pitting corrosion
Hastelloy B-3	66 °C, L	2.84	8.8	Dark gray color. Uneven sponge-like corrosion. Small crevice and pitting corrosion
	66 °C, V	1.87	5.9	Dark gray color. Uneven sponge-like corrosion, especially in stressed area. Crevice corrosion
	79 °C, L	9.98	7.3	Dark gray color. Uneven sponge-like corrosion, especially in stressed area. Crevice corrosion
	79 °C, V	4.55	12	Dark gray color. Uneven sponge-like corrosion, especially in stressed area. Crevice corrosion
	93 °C, L	2.62	65	Dark gray color. Fissures, crevice, and pitting corrosion
	93 °C, V	2.39	25	Ni plated appearance. Fissures, crevice, and pitting corrosion

Figure 10: The mechanism of SCC process of Q345R immersed in 40 wt% hydrofluoric acid at room temperature (Dai et al. 2020a; with permission from Elsevier).

hydrogen adsorption in 1.25% NaF with the pH of 5.5 was proposed (Könönen et al. 1995). This process could be described as fluoride ion firstly degrading the stable passivation film (mainly consisted of TiO_2) and causing it to rupture (de Assis Ferreira et al. 2016). The bottom of the trench would easily induce stress concentration when subjected to tensile load and due to the flow discrepancy of solution inside and outside the trench, the pH of the bottom solution was reduced (Wanhill 1975). Thus, the H atomic generated in the cathodic reaction would be absorbed into the matrix and formed hydrides (Noel et al. 2018; Sato 1990), which then caused cracks to nucleate and expand during subsequent stress corrosion process. The crystal lattice distortion of titanium alloy was severe after cold deformation, which increased the solubility of hydrogen, and in turn contributed to hydrogen-induced stress corrosion brittle fracture (Yokoyama et al. 2004). Although in HF or fluoride ion-containing environment, hydrogen-induced stress corrosion cracking (HISCC) was considered to be a major failure mechanism, the evidence was still insufficient. Especially in HF solution, the corresponding microscopic evidences are rare. Whether the SCC process is dominated by internal penetration of local corrosion or hydrogen-induced failure still needs to be confirmed.

CF is another important issue for material degradation in HF environment. But so far limited reports on corrosion fatigue in HF environment are found. This is largely due to the strong corrosion, volatility, and toxicity of HF solution, making the online cyclic load corrosion fatigue experiment hardly to be conducted. Chen et al. (2020a,b) carried out precorrosion fatigue tests of 316L in HF solution and found that pits formed on the surface during precorrosion were the main sites for fatigue crack initiation. In addition, the corrosion fatigue life was affected by the geometry of pits, and a qualitative relationship between the apparent size of pits and fatigue life was given (Chen et al. 2020a,b). Under service conditions, cyclic loading and corrosion take place at the same time,

and the interaction between these two behaviors makes it more complicated. While for solution containing fluoride ion with acidic environment ($\text{pH} < 6$), similar with the stress corrosion crack mechanism, the brittle fracture mechanism of hydrogen adsorption-induced mechanical degradation was still the dominant process for corrosion fatigue failure of titanium alloys (Correa et al. 2009). The fatigue life was affected by fluoride ion concentration, and the increase in fluoride ion content significantly accelerated the fracture process of Ti and its alloys (Roselino Ribeiro et al. 2007; Yokoyama et al. 2005). Compared to concentration, pH value changed the corrosion fatigue life more significantly. In a neutral environment ($\text{pH} = 7$), even if a large amount of fluoride ion was added (1000–10,000 ppm), there was no difference in the corrosion fatigue life of Ti and its alloys difference, which was due to the low attack of fluoride ion in neutral environment (Guilherme et al. 2005; Zavanelli et al. 2004, 2000).

5 Future prospects

At present, although numerous studies on HF corrosion have been carried out and a certain understanding of the attack behavior of fluoride ion for various metallic materials has been acquired, the research on HF internal corrosion mechanism and quantitative evaluation are still insufficient.

- (1) There are the two views on passivation degradation mechanisms of stainless steels in HF or fluoride ion-containing environment. It is necessary to integrate and unify these two points in order to provide new insights for understanding the corrosion mechanism of stainless steels.
- (2) Alloying elements determine the passivation mechanism of material in HF solution, thus resulting in different corrosion resistance. For Mo element, it is

necessary to explore how excessive Mo content affects corrosion process. In addition to the effect of single isolated alloying element, the interaction between different alloying elements might provide new insights into the different corrosion resistance. In addition, quantitative correlations between alloying elements and corrosion sensitivity need to be developed, which will facilitate rational design of corrosion-resistant material in HF environment.

- (3) The influence of environmental factors on corrosion resistance is significant, and its influencing laws are not single, and an understanding from the perspective of internal corrosion mechanism is useful.
- (4) The stress corrosion and corrosion fatigue tests in HF environment are rarely studied, and multiple damage mechanisms of mechanical–chemical coupling still focused on the apparent phenomenon. The internal failure mechanism is still unclear, especially at micro and nano scales.

6 Conclusion

This manuscript reviewed recent progress on HF corrosion, from the aspects of the attack characteristics of fluoride ion, the corrosion behavior of metallic material in HF or fluoride ion-containing solution and influencing factors, the main conclusion are as follows:

- (1) Compared to other corrosive medium, due to the physical and chemical characteristics of fluoride ion, it has three kinds of special properties, including active dissolution ability, strong affinity and complex form of attack (uniform corrosion and local corrosion), which play an important role in corrosion behavior of metallic materials in HF or fluoride ion-containing environment.
- (2) The corrosion of metallic materials in HF or fluoride ion solution shows a significant passivation weakening process. There are three corrosion mechanisms to describe this process: Fluoride ion induced passive film degradation process, fluoride ion preferentially affiliates with matrix to inhibit passivation process, and the synergetic effect of fluoridation and oxidation.
- (3) In terms of chemical composition, the effects of Mo, Cr, Fe, and Cu elements are discussed, which affect passivation process. The different passive films dominated by various elements show distinct thermal stability, resulting in different corrosion resistance when suffered severe attack from fluoride ion. Besides, the relationship between Mo content and alloying corrosion rate is discussed. The content of Mo is not always favorable for improving alloying corrosion resistance,

which will be reduced when Mo content exceeds a certain value.

- (4) The presence of dissolved oxygen within a certain range in solution enhances the attack by HF, but the corrosion rate of alloys slightly decreases when the content of dissolved oxygen reaches a threshold value. The concentration of HF solution only increases the damage degree by HF other than changes the attack mode. In contrast, temperature activates the internal attack of HF. Corrosion in liquid phase and vapor condition of HF is different, and such a difference is also influenced by the type of metallic alloys. Moreover, in a mixed medium environment, the role of fluoride ion with active dissolving property is always prominent, and fluoride ion is prone to inhibit the change of metastable pit into mature pit (pit initiation) and pit growth.
- (5) Regarding the causes for stress corrosion cracking and corrosion fatigue cracking in HF or fluoride ion environment, in addition to internal penetration caused by local corrosion (based on anodic active dissolution theory), hydrogen-induced material embrittlement is also considered to be an important failure mechanism.

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