The effect of microstructure on corrosion behavior of ultra-high strength martensite steel-A literature review

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Abstract:

The ultra-high strength martensite steels are widely used in aerospace, ocean engineering, etc., due to their high strength, good ductility and acceptable corrosion resistance. This paper provides a review for the influence of microstructure on corrosion behavior of ultra-high strength martensite steels. Pitting is the most common corrosion type of ultra-high strength stainless steels, which always occurs at weak area of passive film such as inclusions, carbide/intermetallic interfaces. Meanwhile, the chromium carbide precipitations in the martensitic lath/prior austenite boundaries always result in intergranular corrosion. The precipitation, dislocation and grain/lath boundary are also used as crack nucleation and hydrogen traps, leading to hydrogen embrittlement and stress corrosion cracking for ultra-high strength martensite steels. Yet, the retained/reversed austenite has beneficial effects on the corrosion resistance and could reduce the sensitivity of stress corrosion
cracking for ultra-high strength martensite steels. Finally, the corrosion mechanisms of additive manufacturing ultra-high strength steels and the ideas for designing new ultra-high strength martensite steel are explored.

**Key Words**: Corrosion behavior; Ultra-high strength; Martensite steel; Microstructure; Additive manufacturing

1. Introduction

Ultra-high strength martensite steels refer to the formation of carbides or intermetallic compounds by adding alloying elements (Ti, Cu, Nb, Al), thereby improving the strength of the alloy, which are widely used in ocean engineering, aerospace, etc. [1, 2]. The high tensile strength (higher than 1380 MPa) and good ductility of ultra-high strength steels mainly derived from the complex heterostructure microstructure, such as martensite, precipitate and small amount of austenite. Simultaneously, the complex heterostructures have an important impact on the corrosion resistance, involving the alloy distribution and interface of heterogeneous [3-6].

The corrosion behavior is more and more important with the increasing of equipment service time and the deterioration of the service environment. The corrosion resistance of ultra-high strength martensite steel mainly comes from high content of chromium (higher than 13%) or complex alloy content, which could result in the thin passive film or oxide film covered on the surface of samples [7, 8]. The thin surface film acts as a barrier between the steel substrate and the corrosive environment, which could prevent further corrosion of the substrate. The stability and protection of the oxide film are important for corrosion resistance [9-11]. However, the complex microstructures (martensite, precipitation, austenite) of ultra-high strength martensite steel could cause the uneven distribution of alloying elements and multiplex interfaces, which result in poor stability of the
passive film and corrosion production film [12, 13]. The corrosion sensitivity always improves and occurs in weak areas of the oxide/passive film [14, 15]. So that it is very important to study the influence of microstructure on corrosion mechanisms and optimize manufacturing process/composition for ultra-high strength martensite steel.

The research on corrosion behavior of ultra-high strength martensite steel has caused widespread concern in the recent year. Based on the previous studies, the progress for the research on corrosion mechanisms of ultra-high strength martensite steel is comprehensively reviewed in the paper. The effect of microstructure on initial corrosion, intergranular corrosion, stress corrosion cracking (SCC)/corrosion fatigue and hydrogen embrittlement (HE) is categorically summarized. The research results could provide the direction for developing of new advanced ultra-high strength martensite steel with better corrosion resistance.

2. Ultra-high strength martensite steel classes and their corrosion mechanisms

2.1 Ultra-high strength martensite steel classes

Ultra-high strength martensite steel usually adds many strengthening elements, leading to the precipitation of carbides, nitrides, carbonitrides and intermetallic compounds in the martensite lath. It not only achieves high strength, but also has good toughness. It can be divided into three types according to the corrosion resistance (low-alloy martensite steel, precipitation hardening stainless steel, maraging stainless steel [16]). In addition, additive manufacturing has been widely used to fabricate ultra-high strength martensite steel, especially precipitation hardening stainless steel [17].

(1) low alloy martensite steel: Low-alloy ultra-high strength martensite steel contains little Mn, Si, and a small amount of Nb, V, Ti, Al or other alloying elements (less than 3%) on the basis of carbon steel. The better corrosion resistance of low-alloy steel is benefit from the surface corrosion
production film. The achievement of high strength mainly come from solid solution strengthening and precipitation hardening. The common low alloy ultra-high strength steels include 300M, Aermet100, 30CrMnSi [10, 18, 19].

(2) Precipitation hardening stainless steel: The carbon content is generally less than 0.1%. It is strengthened by adding hardening elements (copper, aluminum, titanium, etc.). The chromium content is generally 15-17%, which always contains martensitic precipitation hardening stainless steel (such as 15-5PH, 17-4PH, 13-8Mo [4, 20, 21]) and semi-austenitic precipitation hardening stainless steel (such as 0Cr17Ni7, AM355 [22, 23]).

(3) Maraging stainless steel: The carbon content is not higher than 0.03% to ensure the toughness, corrosion resistance, weldability and workability of the martensitic matrix, and the chromium content is not less than 12% to ensure corrosion resistance. There are also some high content alloy elements (cobalt, titanium, nickel), which could precipitate the intermetallics, such as Ni₃Ti, Ni₃Mo, NiAl. The typical maraging steels are Custom 455/465 steel, IN736, Almar362 [24, 25].

(4) Additive manufacturing ultra-high strength martensite steel: The common ultra-high strength martensite steels practically in use by additive manufacturing are 17-4 PH and 15-5 PH [26, 27]. The microstructure of additive manufacturing ultra-high strength martensite steel is special from that of traditional ultra-high strength steel due to non-equilibrium solidification. Some researches indicated that the microstructure of precipitation hardening stainless steel mainly contained thin martensite lath, which involved in manufacturing defects, molten pool interface and so on [28]. The high strength of precipitation-hardening stainless steel by additive manufacturing are comparable to that of traditional process [29, 30]. However, the corrosion behavior of additive manufacturing ultra-high strength martensite stainless steel has not been thoroughly studied. So that it is important to
study the corrosion mechanisms of additive manufacturing ultra-high strength martensite steel in the future.

2.2 Corrosion mechanisms

(1) Uniform corrosion

The low alloy ultra-high strength steel always suffers from the uniform corrosion due to the low chromium content. There is the uniform corrosion production film on the surface of the low alloy steel to prevent further corrosion. The corrosion resistance of the low alloy steel depends on the density and integrity of corrosion production film, which always is affected by the alloy composition and microstructure. So that the effect of alloy composition and microstructure on the corrosion production film and initial corrosion should be studied further.

(2) Pitting

Pitting corrosion (also known as pinhole corrosion) is an extremely localized pinholes corrosion that occurs in localized surface of stainless steel. The local surface of passive film is broken down in the Cl- contained sensitive environment, which results in the pitting as the anode, and the other positions of the passive film are used as the cathode. So that the micro-corrosion cell is formed around the pitting, which is the “small anode, large cathode” region. There are the anode reactions inside of pitting: \( M \rightarrow M^{n+} + n e^- \). Simultaneously, there is the cathode reaction outside of pitting: \( \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \) [9, 13, 19].

The corrosion products (metal oxide) cover on the surface of pitting, resulting in occlusion of the corrosion cell. So that the dissolved oxygen can’t diffuse into pitting and metal ions can’t diffuse outside of pitting. More chloride ions migrate inside of the pitting, resulting in acidification and autocatalytic processes in the pitting. So that once pitting occurs, the dissolution rate is quite large
and it often causes accidents suddenly. Thus, the pitting mechanism of stainless steel has been extensively studied[31, 32]. Pitting corrosion mainly occurs in locations where the stability of the passive film is poor such as inclusion, carbide/intermetallic interfaces.

(3) Intergranular corrosion

Intergranular corrosion is the selective corrosion of stainless steel in sensitive areas, usually due to inappropriate heat treatment, welded joints, etc., Carbides are usually precipitated at the prior austenite grain boundary or the martensite lath, which results in preferential corrosion and has a high sensitivity to intergranular corrosion. So that it always results in fractures along grain boundaries of prior austenite or martensite lath [33, 34].

(4) Hydrogen embrittlement

The high strength of martensite steel is sensitive to hydrogen embrittlement due to the heterogeneous microstructure. The cathodic reaction of corrosion could produce hydrogen during service, which increases the sensitivity for hydrogen embrittlement and premature failure [35]. There are two prevalent mechanisms for hydrogen embrittlement as hydrogen-enhanced localized plasticity (HELP) and hydrogen-enhanced decohesion (HEDE) [36, 37]. The HELP mechanism shows that hydrogen promotes dislocation motion and planar slip, which explains local plasticity and slip zone fracture [38]. HEDE theory believes that hydrogen could cause a reduction in the cohesive bond strength, which generally explains sudden brittle fracture without the obvious deformation [39]. The effect of multiple microstructures on hydrogen embrittlement is more complex and it is very significant to study the hydrogen embrittlement mechanisms of ultra-high strength steel for developing better resistance of hydrogen embrittlement.

Some literatures demonstrated that the resistance of hydrogen embrittlement for martensite steel
was low due to the high strength and complex microstructure [18, 40]. Hydrogen could accelerate crack growth and eventually led to rapid failure for ultra-high strength steel. There are many factors for influencing hydrogen diffusion coefficient and the hydrogen trapping behavior for hydrogen embrittlement, such as microstructure, service strength/environment and heat treatments. The hydrogen could be captured at the metallurgical inhomogeneities (e.g. precipitates, inclusions, dislocations, et al.). So that it is necessary to study the effect of microstructure on hydrogen embrittlement mechanisms [38-40].

(5) Stress corrosion cracking/corrosion fatigue

Stress corrosion cracking and corrosion fatigue are common causes of failure and fracture for ultra-high strength martensite steel. There should be three conditions for the SCC and corrosion fatigue: (1) the service load needs to be above the critical value of stress corrosion; (2) the alloy should be sensitive for the SCC; (3) the sensitive service environments [41]. The typical corrosion environment for SCC of martensite steel showed in Table 1. The mechanism underlying stress corrosion cracking are complex and still matter of debate in the literatures [42, 43]. The main debate about the mechanism of SCC of high strength alloys are focus on the anode dissolution and hydrogen induced cracking (HIC) theory, which are related to the influence of microstructure on the corrosion dissolution and hydrogen induced cracking. So that stress corrosion cracking and corrosion fatigue often occur simultaneously with hydrogen embrittlement, which occasionally cause catastrophic accidents.
Table 1. The typical corrosion environment for martensite steel

<table>
<thead>
<tr>
<th>Materials</th>
<th>Corrosion environment</th>
</tr>
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<tbody>
<tr>
<td>low alloy martensite steel</td>
<td>Solution(NaOH, H₂S,HCl, NH₃, Carbonate, Nitrate), Marine</td>
</tr>
<tr>
<td></td>
<td>and industrial atmosphere</td>
</tr>
<tr>
<td>Martensite stainless steel</td>
<td>Humid air, Aqueous solution, Organic solvent containing water,</td>
</tr>
<tr>
<td></td>
<td>HCN solution</td>
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The corrosion fatigue and stress corrosion cracking of martensite steel suffer from typical aqueous solution and stress loading in service. So that the high strength steel was susceptible to the SCC. Simultaneously, as increasing of the tensile strength of metal, the susceptibility of corrosion fatigue and stress corrosion cracking increased. Thus, the martensite ultra-high strength steel always suffers from the failure by the stress corrosion cracking and corrosion fatigue. Simultaneously, the susceptibility is related to the microstructure of ultra-high strength steel. So that it is very necessary to study the effect of microstructure (inclusion, precipitations, retained austenite) on the corrosion fatigue and stress corrosion cracking in order to optimize the resistance of corrosion failure.

3. The effect of alloy composition

The excellent mechanical properties and moderate corrosion resistance for ultra-high strength martensite steel can be changed by additive alloying elements, such as Cr, Mn, and Co improving the strength and toughness, Ni and Mo improving the toughness, Ti improving the strength but reducing the toughness. The effect of alloying elements on the corrosion behavior of ultra-high strength steels is an important issue to provide guidance to the material design and usage in industry.
field. The alloy elements have important effect on the density of corrosion production film and stability of passive film.

3.1 The effect of alloy composition on the corrosion production film of low alloy steel

Alloying elements could be concentrated in the corrosion product film, which have an important influence on the protection of corrosion products film and corrosion resistance of low alloy steel [44]. Cr as a common element in low alloy ultra-high strength steel is always enriched in the inner layer of the corrosion product film, which can promote the formation of a dense inner layer film, thereby improving the corrosion resistance of low alloy steel [45]. At the same time, the presence of nickel will change the composition and corrosion resistance of the corrosion product layer, which could enrich in the corrosion production film and decrease the defects density. The ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and thickness of inner corrosion production film increased with addition of Ni. So that the nickel addition could promote more protective inner corrosion production film and significantly reduce the corrosion rate [46]. Mo may also enrich in the inner rust layer, produce $\text{MoO}_3$, enhance the formation of compact rust film and impede the anode dissolution reaction [47]. However, the comprehensive effects of different alloying elements on the corrosion film of low alloy ultra-high strength steel should be investigated by high-throughput experiments/simulation methods.

3.2 The effect of alloy composition on the passive film of high strength stainless steel

Martensite ultra-high strength stainless steel contains higher alloying elements (Cr(wt%)≥12%), which can form the nano-thin passive film on the surface of the sample. The alloying elements (such as Cr, Mn, Co, Ni and Ti) could change the chemical composition and density of the passive film. The composition of passive film for ultra-high strength martensite stainless steel is an iron-rich outer
layer (iron oxide) and a chromium-rich inner layer (chrome oxide) [9, 48]. High content chromium of stainless steel could improve the protection and corrosion resistance of the passive film [49]. Huiyan Li et al [50] showed that the inner corrosion products of 0Cr12Ni3Co12Mo4W ultra high strength stainless steel were mainly composed of the oxides of Cr and Mo and the outer layer mainly contained the oxides of Fe, Cr, Mo and Co (Fig.1(a)). As pitting occurred, Fe and Co gradually dissolved and diffused into the solution, while Cr and Mo remained inside of the pitting. Hong Luo et al [51] indicated that there was no Cu detected in the composition of the passive film of rich-Cu precipitation in 15-5PH precipitation hardening stainless steel (Fig.1(b)). Simultaneously, the corrosion resistance decreased with the decreasing of Cr/Fe ratios and increasing in hydroxides in the passive film. In addition, nickel is an important element, usually enriched in the inner layer of the passivation film, which promote the crystallization and improve the corrosion resistance of the passive film according to results by Marcus [52]. Simultaneously, martensite high-strength stainless steel also has a secondary passive film in a specific environment. Cheng Man [11] demonstrated the secondary passive film contained more Fe than that in the metal matrix. The passive film is composed of nano particles and the secondary passive film has nano-scale pores. The secondary passive film exhibits more donor density, with a more passive formation potential.
Fig.1. (a) AES depth profiles for the passive film of the 0Cr12Ni3Co12Mo4W steel formed in 0.1M Na$_2$SO$_4$ solution at pH=3 [50]; (b) the Cu$_{2p}$ results of the passive film for 15-5PH steel by XPS [49].

4. The effect of precipitations

The ultra-high strength martensite steel is mainly strengthened by nano precipitates, such as carbides, intermetallics and so on. The precipitations could cause segregation of alloying elements, which involved in alloy-depleted zones, interfaces between precipitates and matrix, and stress concentration. So that the formation and coarsening of the precipitates has negative effects on the corrosion resistance of ultra-high strength stainless steel [53].

4.1 The effect of precipitation on the pitting

In general, A large amount of carbide precipitations could hinder the regeneration of passive film in martensite stainless steel [54]. The rich-Cr carbides lead to the formation of chromium-depleted zones near precipitates, which usually acts as preferential sensitive sites for pitting corrosion for martensite stainless steel (Fig.2) [55]. Moreover, the nano-sized (Cu, Nb)-rich carbides of 15-5PH stainless steel were observed by atom probe tomography (APT). The Cr content around the precipitates reduced and the pitting corrosion resistance deteriorated for 15-5PH stainless steel [49]. Huiyan Li et al [50, 52] showed that the surface potential of carbides was lower than that of the martensitic matrix. So that the carbides formation always caused the pitting for the Cr12Ni3Co12Mo4W Ultra-High-Strength steels [56]. However, there is little direct evidence for the effect of nano-scale carbides on pitting corrosion by in-situ observation (Transmission Electron Microscope (TEM)).
Fig. 2. TEM images of tempered martensite steel: (a, b) M$_{23}$C$_6$ carbides, (c) SAED pattern from (d) precipitates and (e) matrix, (f) micromorphology (g) pitting around the carbide[54].

As described before, the high strength maraging stainless steel is mainly strengthened by nano-
scale intermetallics, which are distributed in the martensite matrix, such as Ni₃Ti, NiAl, Ni₃Mo [57, 58]. The intermetallics also have an important effect on the corrosion behavior of maraging steel. Li Wang et al. [59] studied the effect of Ni₃Ti precipitates on the corrosion behavior of Custom 465 maraging stainless steel combined TEM samples and Scanning Kelvin probe force microscopy (SKPFM). The surface potential of the precipitate/matrix interface was approximately 30 mV lower than that of the precipitates, which revealed that the interface of precipitates and matrix was sensitive for the pitting (Fig. 3). The interface of Ni₃Ti/matrix may be origin of pitting for maraging stainless steel. The maraging stainless steel will be the most promising development direction for high strength martensite stainless steel due to the intermetallics hardening [24]. So that the effect of intermetallics on corrosion mechanisms should be studied more in the future.
**Fig.3.** SKPFM results of Ni$_3$Ti precipitates: (a) surface morphology of the SKPFM, (b) Local area of (a), (c) surface potential of SKPFM, (d) surface potential of scan line 1[59].

4.2 The effect of precipitation on the intergranular corrosion

The carbides are usually more easily formed at the grain boundary due to the high mismatch and low binding energy. The passive film of Cr-depleted zones near the carbides was unstable and was sensitive for the corrosion. So that the carbides and matrix were the cathodic area, and Cr-depleted zones near carbides and grain boundary were anodic one, which was the corrosion cell with the “large cathode, small anode” [60]. Thus, the intergranular corrosion always occurred at the grain boundary of prior austenite grain boundary. Simultaneously, martensite induced sensitization is another type of sensitized zone susceptible to an intragranular corrosion attack between martensite laths [61, 62]. So that the tempered martensite was more sensitive than the quenched martensite due to the precipitation of carbides as shown in Fig.4 (a) and (b) [62, 63].

Some research showed that the intergranular corrosion always occurred for the weldment, inappropriate aging temperature for ultra-high strength martensite stainless steel [64, 65]. J.M. Aquino et al. [63] studied the intergranular corrosion susceptibility of martensite stainless steel, which showed that the tempered area of the welded joint was more sensitive than the base metal due to the Cr-carbides precipitation in the welded joint. S.S.M. Tavares showed that when the tempered temperature was higher than 495°C, the sensitization of intergranular corrosion for 17-4PH stainless steel was high by DL-EPR experiments, showing obvious intergranular corrosion related with carbides (Fig. 4) [66].
Fig. 4. Microstructures and intergranular corrosion of martensite stainless steel; (a) carbide distributed at the interface of AM355 steel, (b) EDS around the carbide in (a), (c,d) the intergranular corrosion of 17-4PH steel after prepared with 10wt.% oxalic acid solution [66].

4.3 The effect of precipitation on the hydrogen embrittlement

The precipitation of ultra-high strength martensitic steel has complex effect on the hydrogen embrittlement. The carbide precipitation phase always act as a hydrogen trap to reduce the hydrogen embrittlement resistance of martensitic ultra-high strength steel. Hu et al [18] showed that apparent hydrogen diffusivity and steady hydrogen permeation current decreased for tempered Aermet 100 martensite steel, which was attributed to hindering hydrogen diffusion by coherent precipitations (M₂C). With the development of advanced characterization techniques [67], deuterium atoms are observed to the surface of TiC [68] and VC carbide precipitation phases [69] by atom probe...
tomography (APT). Simultaneously, compared to the incoherent precipitation phase [70], the coherent precipitation phase (NbC, VC) is more likely to act as a hydrogen trap for martensite steel [71]. The complicated interface (such as phase boundary, precipitates interface) provided a lot of traps for hydrogen atom for ultra-high strength steel due to the high mismatch [71]. The hydrogen-trapping capability of carbides differs depending on the kind, size and morphology of precipitates. At the same mole fraction, the hydrogen-trapping capability of carbides decreases in the order NbC > TiC > VC > Mo2C. So that, the addition of an alloy element, such as V, Ti, and Nb, in high strength steels was a more effective method for improving the HE resistance due to additional hydrogen trap sites and impeding hydrogen diffusion. The intermetallic is also the precipitation strengthening phase for maraging steel, which also has an important effect on the hydrogen embrittlement. With the formation of the NiAl precipitated phases of 13-8Mo ultra-high strength stainless steel, the tensile strength and the sensitivity to hydrogen embrittlement increased [72, 73]. The incoherent Cu-rich precipitates in 17-4PH steel were more sensitive for the hydrogen traps than the NiAl precipitates of 13-8Mo martensite steel [74]. For Custom 465 maraging steel, there is a local stress concentration near the η-Ni3Ti precipitation phase, which leads to the enrichment of hydrogen atom [72].

In addition, the grain boundary [75] and lath interface [76] also provide trap sites for hydrogen atoms and have important effect on the hydrogen embrittlement. At the same time, higher initial dislocation density formed near prior austenite boundary, which acts as the hydrogen traps due to the apparent elastic strain regime during deformation [77]. So that for ultra-high strength martensite steel, the hydrogen trapping sites contain grain boundaries, lath boundaries, interstitial, dislocations, Cu-rich precipitates or NbC precipitates as shown in Fig.5.
4.4 The effect of precipitation on the stress corrosion cracking/ corrosion fatigue

Carbide precipitates have an important effect on the cracking of stress corrosion and corrosion fatigue. The interface between carbides and matrix is the preferential site for the nucleation and expand for stress corrosion cracking due to the alloy depletion and hydrogen accumulation [78, 79]. In addition, the interface of large-sized titanium nitride precipitates could undergo cracking during the deformation process, which eventually led to crack propagation and hydrogen aggregation for ultra-high strength steel [80]. So that the carbide-free martensite steel has higher corrosion fatigue strength and higher resistance of stress corrosion cracking than carbides strengthening martensite steel [81]. The resistance to corrosion fatigue cracking of overaged ultra-high strength steel was less than that of aged samples at equal strength levels [82].

In addition, the nanosized (Nb,Ti,V)(C,N) precipitates were inferred to act as irreversible traps and reduce the probability of HIC, thereby enhancing the SCC resistance of steel in hydrogen-rich
environments. Some studies showed that small-sized (nano-sized) dispersed carbide precipitates hinder crack propagation and improve stress corrosion resistance [83]. As the aging temperature increased (overaged), the size of carbides increased and localized alloy depletion provided a path for crack growth and promoted stress corrosion crack growth and reduced resistance of stress corrosion as shown in Fig. 6 [84].

![TEM image with the corresponding Energy Dispersive Spectrometer (EDS) elemental maps with carbides for H900-aging treatment of 17-4PH steel (a) and stress–strain plots obtained with carbide (b) and H900 (c) [78].]

Fig. 6. TEM image with the corresponding Energy Dispersive Spectrometer (EDS) elemental maps with carbides for H900-aging treatment of 17-4PH steel (a) and stress–strain plots obtained with carbide (b) and H900 (c) [78].

5. The effect of retained/reversed austenite

The retained/reversed austenite is the second phase of martensite ultra-high strength stainless steel to improve the ductility. The reversed austenite phase is obtained via inter-critical tempering at temperatures slightly higher than the austenite transformation temperature (As). The distributions of elements (especially Cr, Ni, and Mo) in austenite are expected to influence the passivity and

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corrosion resistance of ultra-high strength martensite steels. At the same time, reversed austenite usually nucleates at the Ni-enriched region that exists adjacent to the Cr-rich M$_2$C$_6$ carbides. Therefore, it is crucial to evaluate the effect of reversed austenite on the corrosion resistance of ultra-high strength martensite steel.

5.1 The effect of retained/reversed austenite on the pitting

There is an obvious nickel-rich zone near the carbide, which is conducive to the formation of reversed austenite during aging treatments [85]. So that the formation of the reversed austenite phase could reduce the extent of Cr depletion around the carbides, which could improve the pitting corrosion resistance of ultra-high strength steel [86]. Simultaneously, a higher concentration of Mo and Ni in reversed austenite contributes to a higher pitting resistance of austenite that is adjacent to the carbides, where the Cr depleted zones exist. Thus, the 620°C-tempered specimen of 13Cr martensite stainless steel exhibits better resistance of pitting corrosion due to the presence of reversed austenite [87, 88]. Li Wang et al.[59] studied the effect of reversed austenite on the surface potential for passive film by SKPFM. The surface potential of austenite was 14 mV higher than that of the martensite, which could improve the stability of passive film and enhanced the resistance of pitting for Custom 465 maraging stainless steel. Thus, the presence of austenite could improve the pitting corrosion resistance of martensitic ultra-high strength steel.

5.2 The effect of retained/reversed austenite on intergranular corrosion

The reversed austenite formed near the carbide precipitation phase was contributed to improving intergranular corrosion resistance. Cheng Man et al.[89] found that the reversed austenite formed at the Cr-depleted zone near carbides, which decreased the number of nucleation sites for intergranular corrosion as shown in Fig.7. So that the austenite could inhibit intergranular corrosion.
for semi-austenitic martensite steel. In addition, the reversed austenite is usually formed at the original austenite grain boundary and the martensite lath, which could hinder intergranular corrosion crack propagation. However, the healing effect was not observed in the 600–650 °C range for 17-4PH precipitation hardening steel, which may be due to the limited austenite of 17-4PH stainless steel [66].

Fig.7. The mechanisms of austenite on the intergranular corrosion; (a)TEM image of austenite and carbide, (b) line scanning in (a), (c) the optimization mechanism of austenite on the intergranular corrosion [89].
5.3 The effect of retained/reversed austenite on hydrogen embrittlement

Austenite has strong deformation and high hydrogen storage capacity due to the face-centered cubic structure than martensite microstructure [90, 91]. It has a relatively high binding energy of 55 kJ/mol for irreversible hydrogen trapping site [92, 93]. So that the austenite has great effect on the hydrogen embrittlement for ultra-high strength martensite steel due to its high hydrogen solubility and low hydrogen diffusivity. Y.S. Ding et al. [94] showed that the resistance of hydrogen embrittlement was better for 13-8Mo martensite steel tempered at higher temperature, which was attributed to the formation of reversed austenite. The reversed austenite acted as a trap for hydrogen, hindering the diffusion of hydrogen to the crack tip (Fig. 8). The reversed austenite near the stress concentration area has been transformed into new martensite, which could reduce the stress concentration and thus improved the resistance to hydrogen embrittlement. The cracking occurs at the boundary of martensite lath and new martensite interface. The cracking along the boundaries is supposed to be associated with the different hydrogen redistribution processes, which can be understood by the synergistic interplay of the HELP and HEDE mechanisms for hydrogen-assisted fracture. Simultaneously, the reversed austenite transformation required certain hydrogen content and plastic deformation. The reversed austenite transformation occurred around 200 nm at the crack tip, so its beneficial effect was limited (Fig.9) [33]. However, some studies showed that austenite could accelerate the hydrogen embrittlement failure of ultra-high strength martensite stainless steel or welded martensitic steels [37, 95]. The transformed fresh un-tempered martensite associated with the reversed austenite is most susceptible to hydrogen embrittlement. This is mainly related to the stability of the second phase austenite and the enrichment degree of hydrogen atoms, which is important to the microstructure optimization for better hydrogen embrittlement. So that the effect
of reversed austenite on the hydrogen embrittlement for ultra-high strength martensite steel should be further verified.

Fig. 8. APT atom maps of martensite stainless steel. (a) APT results of Ni, Cr, Mo, C and H; (b) APT results of Ni and H with a selected cylinder; (c) the chemical composition of H, C, Ni and Cr measured using line in (b) [33].
Fig. 9. TEM results of cracking tips after hydrogen charge. (a) the position of the TEM experiments; (b)TEM images of cracking tips; (c) EDS elemental mapping of Ni in 9b; (d) EDS elemental mapping of Fe in 9b [33].

5.4 The effect of retained/reversed austenite on the stress corrosion cracking

The retained austenite could decrease the sensitivity of stress corrosion cracking for ultra-high strength martensite steel [96]. The austenite is much less effective as a mechanical barrier at the crack tip during initiation since the crack tip opening displacements are high enough to cause local rupture of the austenite during crack growth [97]. Simultaneously, it can act as an "energy trap" and hydrogen trap, decreasing the mechanical driving force available to the crack tip and thereby raising
the apparent stress intensity necessary to initiate growth of a crack [98].

6. The effect of inclusion

In the steel-making process, impurity elements of sulphur and oxygen are difficult to be removed thoroughly, even though the modern ultra-high strength steel-making technique can well control the amount of oxygen and sulphur. Oxygen and sulphur in ultra-high strength steel are usually present in the form of oxide inclusion (Al₂O₃, CaO, SiO₂), manganese sulphide (MnS) [99]. The inclusions always are harmful for the corrosion resistance of ultra-high strength martensite steel.

There are four possible ways in which inclusions might initiate localized corrosion: (1) the inclusion is unstable in the environment, but the matrix is stable (insoluble), or covered by a protecting film; (2) certain phases of the inclusion are unstable, but the matrix is stable; (3) the inclusion is cathodic to the alloy matrix, causing preferential dissolution of the matrix in the vicinity of the inclusion (this condition could also be caused by the local attack at the edge of an otherwise protective film); and (4) the inclusion is disbonded from the matrix, thereby forming an incipient crevice to initiate localized corrosion.

6.1 The effect of inclusion on the pitting/initial corrosion

The inclusions play an important role on alloy element distribution and local stress concentration, which have important effect on the corrosion behavior. S.S.M. Tavares et al. studied the effect of sulfur content on the corrosion resistance of 17-4PH stainless steel. As the sulfur content increased, the degree of sensitization (DOS) measured by DL-EPR tests was obvious for high-sulfur steel. There are a lot of MnS inclusions in the high-sulfur steel. The pitting corrosion occurred preferentially in MnS inclusions, which has been associated with the pitting/initial mechanism (MnS) of low alloy ultra-high strength steel and austenitic stainless steel [100, 101].
Simultaneously, there is the Cr-depleted zone around the Cr-rich oxide inclusion of 17-4PH stainless steel. The pitting corrosion usually nucleated in the Cr-depleted zone. As the pitting continued to expand, Cr-rich oxide inclusions gradually fall off [102, 103]. Simultaneously, C. Man et al. [104] studied the inclusion classes and its effect on the pitting corrosion of AM 355 precipitation hardening stainless steel as shown in Fig.10. It showed that the MnS-(Cr, Mn, Al)O duplex inclusions are more sensitive for pitting corrosion than individual MnS and (Cr, Mn, Al)O inclusions. The Volta potential of MnS was 35 mV lower than that of matrix. The dissolution extends toward the center of the MnS segment until the MnS wears off due to Cr-depleted zone, leaving a crevice adjacent to the (Cr, Mn, Al)O part. The deterioration of the local environment makes the formed crevice expand along the (Cr, Mn, Al)O/matrix interface, which promoted the metastable to stable pitting for duplex inclusion. So that it is necessary to control the formation of duplex inclusions for better resistance of pitting corrosion. Simultaneously, some rare-earth (RE) elements are added in the low alloy ultra-high strength steel for improving mechanical behavior and corrosion resistance. The RE elements could combine with the oxide inclusions, which decreased the sensitivity of the pitting corrosion. At the same time, the RE oxide inclusion always dissolve from the periphery to the middle [105].
Fig. 10. The SKPFM results of duplex inclusion: (a) SEM image, (b) EDS results of duplex inclusion, (c) height image of SKPFM, (d) height analysis for the duplex inclusion (e) surface potential of duplex inclusion, and (f) surface potential of line in (e) [104].

6.2 The effect of inclusion on hydrogen embrittlement

Hydrogen was brought into the metal during smelting and service, which was mainly concentrated in the zones of maximum stress, such as the interface of matrix and hard inclusion (Al₂O₃ inclusion) [106]. When the hydrogen concentration reaches a critical value, crack can
potentially initiate at matrix-hard particle interfaces. According to previous research [107], MnS inclusions are sensitive to hydrogen embrittlement. MnS inclusions have a helpful effect as hydrogen sinks [108]. Therefore, it is necessary to diminish the sulphur level in the ultra-high strength martensite stainless steel for increasing the resistance of hydrogen embrittlement.

6.3 The effect of inclusion on stress corrosion cracking/corrosion fatigue

Some research showed that brittle inclusions were more sensitive to stress corrosion cracking due to difficult deformation [109]. Simultaneously, as the size of inclusions decreased, crack initiation was difficult and the sensitivity to stress corrosion decreased [110]. When the size of inclusions was above 30 μm, cracks initiated near non-metallic silicate inclusions and the corrosion fatigue strength reduced for maraging steel [111]. The initiation of cracking is caused by decohesion of the interface between inclusion and matrix. The final fracture occurs by the main crack consuming the inclusions ahead of it by the “unzipping” of the shear band produced between the crack tip and the inclusion ahead [112].

7. The effect of grain size/boundary, dislocation

The microstructure of ultra-high strength martensite steel contains martensite matrix, austenite, precipitates and inclusion, which involved in grain boundary and multi-interface. Simultaneously, there are many dislocations distributed in the martensite laths. The effect of grain size/boundary, dislocation on the corrosion behavior was complicated, which should be studied by the in-situ observation in the future.

7.1 The effect of grain size/boundary, dislocation on the corrosion behavior

The deformation and heat treatment always involve in the grain size/boundary and dislocation of ultra-high strength steel, which have complex effect on the corrosion behaviors. Wilasinee
Kingkam et al. [113] showed that as the deformation temperature increased, the grain size increased and the corrosion resistance decreased. The pitting corrosion mainly occurred from the interface of high-energy regions. In addition, the grain boundary and dislocation density have important effect on the corrosion resistance by results of electron backscatter diffraction (EBSD). The energy of high angle grain boundary (HAGB) mainly arises from the dislocation energy, and the dislocation density is closely related to orientation differences among grains [114]. The corrosion rate of the steel increases with increasing HAGB frequency. For instance, some studies demonstrated an increase in threshold stress intensity with an improvement in austenite grain size, while others reported no grain size effect [115]. So that the effect of grain size/boundary on the corrosion need to be further discussed. The electrons around dislocation were more active and the energy barrier for corrosion decreased. So that the dislocations were sensitive for the corrosion. As the strain increased, the more cracking generated from the dislocation for the severe deformation [116].

7.2 The effect of grain size/boundary, dislocation on the hydrogen embrittlement/stress corrosion cracking

Related research showed that grain refinement could significantly improve the hydrogen embrittlement resistance benefit from the increasing of proportion of grain boundary of martensitic ultra-high strength steel [117]. Generally speaking, the grain boundary acted used as the main location of the hydrogen trap, which could hinder the diffusion of hydrogen atoms to the crack tip and decrease sensitivity to hydrogen embrittlement [118]. At the same time, the behavior of mobile dislocations of ultra-high strength steel is related to the hydrogen transportation. In addition, high dislocation density is one of the factors which control the strength of a ultra-high strength steel [119]. As the quenching temperature increased, the size of the original austenite grains increased and the
sensitivity to high-strength steel stress corrosion decreased [120].

8. The corrosion behavior of additive manufacturing ultra-high strength steel

Corrosion is an important indicator for evaluating an emerging additive manufacturing ultra-high strength steel. Some studies showed that when printing defects were eliminated, the corrosion resistance of additive manufacturing ultra-high strength stainless steel was better than that of wrought material by polarization test, which was benefit from the refined microstructure during fast cooling of additive manufacturing process [29]. At the same time, there were unique microstructure for additive manufacturing ultra-high strength martensite steel, which involved in molten pool boundary, multi-phase interface and complex particles.

8.1 Effect of manufacturing process on corrosion behavior

The manufacturing parameters have an important effect on the manufacturing defects, which could decrease the corrosion resistance for ultra-high strength martensite steel. Harish Irrinki et al. [121] reported that when the energy density was increased from 64 to 104 J/mm$^3$ for 17-4PH stainless steel, the density and corrosion resistance increased by coarser water-atomized (D50 = 24 and 43 μm) powders. Simultaneously, the fine powders (D50=13~17 μm) was contributed to the better corrosion resistance. Li Wang [28] also showed that the manufacturing defects had an important effect for the corrosion resistance of selective laser melting 15-5PH steel. The pitting mainly originated from the manufacturing defects (Fig.11). So that it is very necessary to explore the appropriate manufacturing parameters to achieve full density for better corrosion resistance.

At the same time, the microstructure of different manufacturing planes for additive manufacturing metals was completely different due to the molten pool and different thermal histories during the printing process. The corrosion behavior of different manufacturing planes was
studied for the additive manufacturing maraging stainless steel. There were the large martensite laths size, low dislocations, low angle grain boundary on the side plane (parallel to the building direction), which was contribute to the better corrosion resistance compared to the top plane (perpendicular to the building direction) [122].

Fig. 11. The effect of manufacturing defects on the corrosion behavior of additive manufacturing 15-5PH stainless steel after corrosion immersion [28].

8.2 Effect of heat treatment on corrosion behavior

In order to get the ideal strength, the additive manufacturing ultra-high strength steel need to be post-heat treated. After aging treatment, Cu-rich nanoparticles (about 10 nm) diffusely precipitated, and approximately 18~25% austenite was distributed near the molten pool boundary. The surface potential of the austenite was approximately 15 mV higher than that of martensite by scanning Kelvin probe force microscopy. However, the austenite phase disappeared and the new NbC-(Mn, Si)O duplex particles precipitated after solution treatment and aging treatment, which decreased the
pitting corrosion resistance and passive film stability of the selective laser melting 15-5PH stainless steel [123]. Simultaneously, the corrosion resistance of as-built samples was the worst. When the aging temperature increased, the corrosion resistance decreased due to the precipitation and coarsening of Cr$_2$C$_6$ particles (Fig. 12) [124].

![Graph showing corrosion current density](image)

**Fig. 12.** The corrosion current and corrosion behavior of selective laser melting 15-5PH steel after
different heat treatments.

9 Conclusion

Ultra-high strength martensite steels are usually used as fasteners, bearing and load-bearing parts in key products in aerospace, marine engineering, nuclear industry, etc. Corrosion behavior becomes more important as the increasing of service time. The effect of microstructure on corrosion mechanisms of ultra-high strength martensite steel is reviewed in detailed. The main conclusions are described below.

(1) The alloy elements always enriched in the inner layer of corrosion production film/passive film could improve the compactness and optimize the composition, which increased the corrosion resistance for ultra-high strength martensite steel.

(2) The retained/reversed austenite has beneficial effects on the pitting corrosion resistance and intergranular corrosion and could improve the resistance of stress corrosion cracking for ultra-high strength martensite steel.

(3) The formation of carbides/intermetallics precipitates always decreased corrosion resistance of ultra-high strength stainless steel due to non-uniform distribution of alloy elements. The stability of passive film on the interface of precipitates/matrix is unstable due to alloy-depleted. The intragranular corrosion attack of high strength stainless steel occurs due to the Cr-depleted area near chromium carbide precipitation.

(4) The pitting/initial corrosion and hydrogen trapping sites of ultra-high strength steel always occurs at weak area of passive/oxide film such as inclusion, dislocations, lath boundaries, grain boundaries, carbide precipitates, intermetallics.

(5) The corrosion resistance of additive manufacturing martensite steel is better than that of
traditional, which is attributed to high content austenite and finer lath martensite. The manufacturing defects and heat treatments have important effect on the corrosion behavior.

10 Outlook

Ultra-high strength martensite steel is an ideal direction for the development of advanced alloys in the future. At present, research on corrosion mechanisms of ultra-high strength martensite steel is still very limited. Through the review conducted in this paper, the problems to be solved and research prospects regarding corrosion mechanisms of ultra-high strength martensite steel are put forward.

(1) The comprehensive mechanisms of alloying elements on the corrosion behavior of martensite steel have not been systematically studied. So that it is necessary to discuss the effect of alloy elements by high-throughput experiment or simulation methods (Materials Genome Engineering).

(2) There are few direct evidences about the effect of nano-scale precipitation (carbides, intermetallic) on the pitting and hydrogen traps. Researchers should develop some advanced in-situ observation technique, such as environmental transmission electron microscope, SKPFM.

(3) Research on the intergranular corrosion of ultra-high strength martensite steel is not systematic and comprehensive. The specifications should be formulated for the possibility of intergranular corrosion of high strength stainless steel. Simultaneously, it is necessary to study the prediction model for stress corrosion/corrosion fatigue crack growth.

(4) There are few studies on the corrosion behavior of additive manufacturing ultra-high strength martensite steel. In order to ensure the safe use of additive manufacturing alloys, the effect of special microstructure on the corrosion need to be studied, such as molten pool interface,
metastable austenite. Simultaneously, it is worth thinking about developing new high strength stainless steel by additive manufacturing.

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