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**Intergranular Corrosion Behavior of Low-Chromium Ferritic Stainless Steel
without Cr-Carbide Precipitation after Aging**

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Highlights:

- Low-chromium ferritic stainless steels are susceptible to intergranular corrosion without precipitation of Cr-carbides at grain boundaries.
- The Cr-depleted zone at grain boundaries induced by Cr-C co-segregation acts as micro-anode and corrodes preferentially.
- The proposed intergranular corrosion mechanism is different from the conventional Cr-carbide precipitation induced sensitization mechanism.

Abstract

The intergranular corrosion behavior of the low-chromium ferritic stainless steel without Cr-carbide precipitation was investigated by the methods of qualitative and quantitative corrosion testing and microstructural analysis. The intergranular corrosion susceptibility of the aged stainless steels can be attributed to the Cr-depleted zone formation induced by Cr-C co-segregation to grain boundaries before Cr-carbide nucleation. The change of intergranular corrosion morphology after aging at 450°C from discontinuous (aged for 2 h) to semi-continuous (aged for 20 h) and to continuous (aged for 200 h) is discussed in detail.

Key words: Ferritic stainless steel; Intergranular corrosion; Segregation; Cr-Carbide; Aging

1. Introduction

Intergranular corrosion (IGC) has been extensively investigated for many years due to its harmful effect on corrosion resistance and mechanical properties of the ferritic stainless steels, which has caused major economic losses to the society [1-3]. The chromium depletion theory of IGC is widely accepted for the ferritic stainless steels [4-11]. This conventional sensitization theory is based on the concept that the susceptibility to IGC is induced by the Cr-depleted zone along the grain boundaries due to the precipitation of Cr-rich carbides during the thermal treatment [10-12]. The Cr-depleted zone acts as the micro-anode and will be preferentially dissolved rapidly in the aggressive media [9, 11] if the Cr content in the depleted zone is less than that required to maintain passivity [6, 8].

The formation of the Cr-depleted zone caused by the precipitation of Cr-rich carbides at grain boundaries has been widely studied during the past few decades [4-11]. It was recently reported by Kim et al. that Cr-depletion occurs due to the segregation of un-reacted Cr atoms around the carbides of the stabilizing elements (Ti or Nb) along the grain boundaries, but not due to the formation of Cr-rich carbides [12-20], which extends the understanding of the mechanism of IGC. Both the conventional sensitization theory and the mechanism proposed by Kim et al. agree with the deleterious effect of the carbides, Cr-rich carbide or carbides of the stabilizing elements (Ti, Nb), on the formation of Cr-depleted zone leading to IGC. However, the susceptibility of the ferritic stainless steels to IGC without grain boundary carbides is still unclear.

Recently, the radiation-induced segregation or depletion of Cr at grain boundaries in nuclear materials of ferritic and austenitic stainless steels have generated considerable research interest [21-35]. It was reported by Marquis et al. that the radiation-induced depletion of Cr in the ferritic stainless steels is observed by atom probe tomography (APT) when the grain boundaries are segregated with Cr and C in the absence of Cr-carbide phase [21-24]. The co-segregation of Cr and C at the grain boundaries has been reported in many nuclear materials of austenitic stainless steels without grain boundary carbide precipitation after aging [36-40]. However, the behavior of IGC without carbide precipitation has not been investigated sufficiently, and remains an important safety issue of nuclear materials.

This paper focuses on the IGC susceptibility of the low-Cr ferritic stainless steel without carbide precipitation at grain boundaries after aging. The IGC performance was investigated by the immersion and electrochemical corrosion testing, including the double-loop electrochemical potentiokinetic reactivation (DL-EPR) and potentiostatic polarization testing. The tests enabled the qualitative and quantitative analysis of the IGC susceptibility. The mechanism of IGC without carbide precipitation is proposed based on the characterization of the grain boundaries using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning Kelvin probe force microscopy (SKPFM).

2. Experimental

2.1. Materials and heat treatment

The investigated steel was prepared as a 10 kg ingot in the laboratory by vacuum melting. The ingot was hot rolled (heated up to 960°C) to 2 mm thick sheet with the chemical composition listed in Table 1. The sheet was then sectioned into samples with the dimension of 95 mm × 39 mm × 2 mm. The samples were annealed at 1050°C for 10 min followed by air cooling. The as-annealed samples were encapsulated in quartz tubes, which were evacuated and backfilled with argon, and subsequently solution treated at 1300°C for 10 min. The samples were directly quenched by cracking the quartz tubes in water as soon as the solution treatment was completed. Afterwards, the samples were cut into small specimens with the dimension of 11 mm × 11 mm × 2 mm and then aged at 450°C for 0 h, 2 h, 20 h, and 200 h.

2.2. IGC testing

IGC tests were conducted in a modified Strauss test solution (0.5 wt% H₂SO₄ + 6 wt% CuSO₄) developed by Devine and Drummond [41] for assessing the degree of sensitization of low-Cr ferritic stainless steels (10-13 wt% Cr). Reduction of the concentration of H₂SO₄ of the standard solution (ASTM A763 and A262) from 16 wt% to 0.5 wt% was to prevent the intense general corrosion. The specimens (11 mm × 11 mm × 2 mm) of each aging time were ground with silicon carbide abrasive paper to #2000, then electro-polished in a solution of 60 vol% H₃PO₄ + 40 vol% H₂SO₄ at a current density of 2 A/cm² for 5 min to facilitate easy identification of IGC attack. Prior to immersion, the specimens were cleaned with deionized water and ethanol in an ultrasonic bath. The specimens were subsequently immersed for 20 h in the 300 ml of

the boiling modified Strauss test solution. The surface of the specimens was closely contacted with copper balls in the solution to produce the effect of galvanic coupling which accelerates the corrosion rate in the test. After 20 h immersion period, the specimens were removed from the solution and rinsed with deionized water and dried. Before their weight losses were measured, a brief immersion in concentrated nitric acid at room temperature for 3 min was made to remove the adherent copper attached on the surface of the specimens. For each aging time, the weight losses were measured by three specimens to obtain the average value of three data points. Additionally, the corrosion morphology of the specimens was observed by SEM (FEI Philips XL30 ESEM FEG) after the corrosion tests.

2.3 Electrochemical corrosion testing

DL-EPR test is a widely used technique [42-44] to quantitatively assess the IGC susceptibility of low-Cr ferritic stainless steels. This test was conducted with a three-electrode system where the sample, a platinum sheet, and a mercury sulfate electrode (MSE, $E = +0.616\text{V}$ vs. SHE) served as the working electrode, counter electrode, and reference electrode, respectively. The mechanically polished specimen with exposed area of about 1 cm^2 was initially scanned from the open-circuit potential and reversed at $+1.2\text{ V}$ (versus open-circuit potential) with the scan rate of 1 mV/s in the electrolyte of $0.05\text{ mol/L H}_2\text{SO}_4 + 0.0005\text{ mol/L KSCN}$ at 30°C . The test was finished at the open-circuit potential where the scan was originally initiated. In this experiment, the scan rate of 1 mV/s was lower than 1.67 mV/s reported by Kim et al. [12] and Park et al. [20]

ensuring that the passive film on the Cr-depleted zone along the grain boundaries could be fully reactivated during the reverse scan loop. Similarly, the higher concentration of KSCN provides the sufficiently aggressive corrosion attack and good selectivity [45]. In the period of anodic polarization scan loop, the current density was continuously increasing until the passive film starts to form (including matrix and grain boundaries) at the passivation potential, from where the activation peak current density (I_a) is determined. By contrast, during the reverse scan loop, the current density reached the smaller reactivation peak current density (I_r), where the Cr-depleted zone along the grain boundaries dissolved, whereas the matrix still stayed passivated. The degree of sensitization (DOS) to IGC of each specimen was evaluated by the ratio of I_r/I_a . For each aging time, the DOS was measured by two specimens and each specimen was examined for three times by DL-EPR, which means that the DOS was the average value of 6 data points. However, it should be noted that the DOS is dependent chiefly on the chemical composition and microstructure of the material in working electrode and on the temperature and concentration of electrolyte, and on the scan parameter [44, 46]. There is not a standard of the test condition in regard to electrolyte and scan parameter. Consequently, it's not acceptable to compare the DOS under different test conditions among different researches. The development of the DL-EPR testing method is completely described and analyzed by Cihal et al. [47].

In order to clarify the type of corrosion which occurred at the multiple peaks of current density during the reverse scan loop, potentiostatic polarization experiments were conducted using the same three-electrode system and the same electrolyte as for

DL-EPR tests. Prior to the potentiostatic polarization at the reactivation current peak potential (E_r) for 2 h, the specimens were passivated at a noble potential for 10 min to simulate the process of passivation in the DL-EPR test. Moreover, the type of corrosion of the specimens was examined by using optical metallography (OM) after potentiostatic polarization.

2.4 Microstructural characterization

The specimens of each aging time etched by Vilella's reagent (1 g picric acid + 100 ml ethanol + 5 ml HCl) were characterized by SEM with energy dispersive X-ray spectroscopy (EDS) and SKPFM (Bruker's Dimension Icon Atomic Force Microscope). SKPFM was used for the simultaneous mapping of topography and determination of Volta potential distribution on the metal surface in air [48-50]. The values of Volta potential were measured relative to the Pt/Ir coated silicon tips with the mode of PeakForce KPFM-AM. It has been reported that the Volta potential measured in air for pure metals is linearly associated with the open-circuit corrosion potentials measured in aqueous solutions [48]. The aged specimens were further investigated using TEM (JEM-2100 operated at 200 kV) with EDS and the scanning TEM (STEM) mode. TEM samples were prepared by mechanically grinding to about 50 μm and then dimpling down to 10 μm followed by ion polishing (Gatan PIPS Model 691).

3. Results and Discussion

3.1 Microstructure of steels

It is generally accepted that IGC of ferritic stainless steels is due to the depletion of Cr along the grain boundaries caused by the precipitation of Cr-rich carbides at the grain boundaries [5, 6, 51]. The Cr-rich carbides are usually observed after sensitization at aging temperatures between 400°C and 700°C [51, 52]. In our study, the specimens were aged at 450°C for 0 h, 2 h, 20 h, and 200 h. The microstructure of the specimens for each aging time etched by Vilella's reagent was observed by SEM. Fig. 1 shows the microstructures of the specimens aged at 450°C for various aging times. Fig. 1 (a) indicates that the grain boundaries of the solution-treated specimens (aged for 0 h) were extremely clean without any precipitation which is consistent with the results reported in the literature [12, 51]. However, with the aging time increasing from 2 h to 200 h there was still no carbide precipitation at the grain boundaries as illustrated in Fig. 1 (b) – (d), which is not consistent with the results in the literature [12, 51, 52]. Therefore, these specimens are not in accordance with the conventional Cr-depletion sensitization theory, namely the precipitation of Cr-rich carbides at the grain boundaries. The IGC susceptibility of the aged steels cannot therefore be clarified based on the conventional sensitization theory and needs to be further investigated. However, it is worth noting that the precipitates can be too fine to detect with SEM considering the fact that the resolution of SEM typically is about 1 μm laterally and in depth.

3.2 IGC testing

To examine the IGC susceptibility of the investigated steel, the specimens aged at 450°C for 0 h, 2 h, 20 h and 200 h were immersed for 20 h in the boiling modified

Strauss test solution. After the IGC test, the corrosion morphology of the samples was observed by SEM and their weight losses were measured. Fig. 2 displays the corrosion morphology of the specimens aged at 450°C for various aging times and plots the IGC rate as the function of the aging time. When the specimen was aged for 0 h (solution treated), the grain boundaries were slightly corroded in the form of small pits distributed sporadically along the grain boundaries and the matrix was nearly uncorroded as shown in Fig. 2 (a). The corrosion morphology is in accordance with the result that the IGC rate of the specimens aged for 0 h was not zero but 0.0712 mg/cm²/day as plotted in Fig. 2 (e). When the specimen was aged for 2 h, the grain boundaries were susceptible to localized IGC in the form of corrosion ditch distributed discontinuously along the grain boundaries and the matrix exhibited slight pitting corrosion as illustrated by Fig. 2 (b). The IGC rate of the specimens aged for 2 h was 0.1597 mg/cm²/day, which is a little higher than that of the specimens aged for 0 h as indicated in Fig. 2 (e). After aging for 20 h, the IGC rate of the specimens increased gradually to 0.3787 mg/cm²/day as shown in Fig. 2 (e). Fig. 2 (c) shows that the grain boundaries exhibit semi-continuous IGC, which means that the corrosion ditch is distributed semi-continuously along the grain boundaries. The matrix was attacked by heavy pitting corrosion distributed densely over the surface. When aged for 200 h, the IGC rate increased sharply to 1.0773 mg/cm²/day (see Fig. 2 (e)). Fig. 2 (d) reveals that the grain boundaries have undergone continuous IGC with the corrosion ditch distributed continuously along the grain boundaries and the matrix is covered with a black film and attacked by slight general corrosion.

Based on the corrosion morphology and the IGC rate, qualitative and quantitative analyses were applied to detect the IGC susceptibility of the investigated steel. By using the weight-loss method to calculate the IGC rate, the IGC susceptibility of the steel is clearly and quantitatively characterized. This is in spite of the fact that the weight-loss method measures not only the rate of IGC but also the rate of pitting corrosion and general corrosion. Nevertheless, it is evident that the aged steel is susceptible to IGC and the susceptibility increases with increasing aging time. The effect of aging time on IGC susceptibility has been investigated [12, 16, 45, 51], showing that the susceptibility increases with increasing aging time for the low-Cr ferritic stainless steels. However, the new finding that the sensitization to IGC of the aged specimens was proved without the carbide precipitation along the grain boundaries still needs to be further investigated.

3.3 Electrochemical testing

To further investigate the new finding, DL-EPR test was applied to assess the DOS of the specimens aged at 450°C for various aging times. The DOS to IGC of each specimen were measured by the ratio of I_r/I_a . Fig. 3 exhibits the curves of DL-EPR results for the aged specimens. At the beginning of the anodic polarization scan loop, the current density continuously increased until the passive film started to form at I_a where the potential was designated as E_a . The values of I_a for the specimens aged at 450°C for different aging times were roughly the same. With increase in the potential, the current density decreased to a relatively stable value, the so-called passive current density, where the passive film formed completely on the surface of the specimens.

After reversing the potential scan, the current became unstable and reached a first weak peak of current density (several $\mu\text{A}/\text{cm}^2$). The current around the weak peak was a negative current (the potential designated as E_{-r1}) as was confirmed by the experimental raw data, meaning that the current around E_{-r1} was not an anodic but a cathodic current. The occurrence of the cathodic current peak is associated with a cathodic reduction reaction, which is not the focus of this article but may be further discussed later. Nevertheless, the weak peak cannot be regarded as I_r , which is supposed to be the anodic current density corresponding to IGC. Thus, the reverse scan curve of the specimen aged for 0 h (solution treated) only showed one weak peak of cathodic current but did not show a reactivation current peak, and therefore the value of I_r was taken as zero. The reverse scan curves of the other three aged specimens showed strong peaks (several mA/cm^2) of I_r , and the currents were anodic currents. The values of I_r were dramatically different, and significantly dependent on the aging time. The specimen aged for 2 h showed only one reactivation peak designated as E_{+r2} . The specimen aged for 20 h showed two reactivation peaks designated as E_{+r2} and E_{+r3} . The specimen aged for 200 h showed one reactivation peak designated as E_{+r3} . For the two reactivation peaks that occurred with the specimen aged for 20 h, it is difficult to calculate the ratio of I_r/I_a . Only the reactivation peak corresponding to IGC can be treated as I_r to calculate the DOS.

In order to prove that IGC occurred at the reactivation peak around the potential of E_{+r2} or E_{+r3} , potentiostatic polarization experiments were conducted. Prior to the potentiostatic polarization, the samples were passivated at a noble passive potential for

10 min to simulate the process of passivation in DL-EPR test. Then the specimens were polarized potentiostatically at the potential of E_{+r2} or E_{+r3} for 2 h. Fig. 4 shows the corrosion morphology of the aged specimens after the potentiostatic polarization at E_{+r2} or E_{+r3} for 2 h. It can be seen in Fig. 4 (a) that IGC attack has occurred along the grain boundaries of the specimen aged for 2 h after potentiostatic polarization at E_{+r2} , which proves that the reactivation peak at the potential of E_{+r2} can be treated as I_r . For the specimen aged for 20 h with two reactivation peaks, IGC attack was observed along the grain boundaries both at the potential of E_{+r2} and E_{+r3} as shown in Fig. 4 (b) and (c). However, the ditch structure of the IGC attack at E_{+r2} was a little wider than that at E_{+r3} and the current density of E_{+r2} was obviously higher than that of E_{+r3} , as evident in Fig. 3. Hence, the reactivation peak at the potential of E_{+r2} was chosen as I_r for the specimen aged for 20 h. For the specimen aged for 200 h, the reactivation peak at the potential of E_{+r3} can be treated as I_r because of the occurrence of IGC attack along the grain boundaries as displayed in Fig. 4 (d).

Based on the results of the potentiostatic polarization, values of I_r for each aged specimen were determined. Thus, the ratio I_r/I_a can be calculated to assess the DOS of the aged specimens. The relationship between the values of DOS and the aging time is plotted in Fig. 5. It can be seen that the value of DOS increased strongly with increasing aging time from 0 for the solution-treated specimen to 15.3% for the specimen aged for 200 h. The value of DOS for the solution-treated specimen was zero because the value of I_r was zero with the absence of the reactivation peak. However, the values of DOS for the other three aged specimens were all higher than 3% and these specimens were

all susceptible to IGC, which is in good agreement with the result of corrosion morphology as illustrated by Fig. 2. Thus, it further proves that the aged steel is susceptible to IGC and the susceptibility increases with increasing aging time. It is noteworthy that the DOS is a relative value based on the current test condition. However, the DL-EPR method still can be employed to investigate the IGC susceptibility and the increasing trend of the susceptibility in combination with the potentiostatic polarization tests.

By conducting the electrochemical DL-EPR and potentiostatic polarization tests, we can state that the aged steel is susceptible to IGC even without any precipitation along the grain boundaries. However, the spatial resolution limitation of SEM may hinder the detection of very fine precipitates. TEM and STEM with the higher spatial resolution were used to characterize the grain boundaries at the nanoscale.

3.4 Characterization of grain boundaries

3.4.1 TEM

In order to characterize the grain boundaries at the nanoscale, TEM and STEM with EDS mapping were employed to detect the precipitation and element distribution in the vicinity of the grain boundaries. Fig. 6 shows the bright field TEM images of the grain boundaries of the specimens aged at 450°C for various aging times. For the solution-treated specimen (Fig. 6 (a)), the grain boundaries were very clean without any precipitation, which is consistent with the microstructure observed by SEM (Fig. 1(a)) and results reported in the previous studies [12, 51]. However, with the increase of the

aging time from 2 h to 200 h (Fig. 6 (b)-(d)), there was still no carbide precipitation observed along the grain boundaries even at the nanoscale, which is consistent with neither the conventional sensitization mechanism [5, 6, 51, 52] of IGC nor the mechanism proposed by Kim et al. [12, 13, 16]. It is generally held by the conventional sensitization mechanism that IGC of the ferritic stainless steels is due to the Cr-depletion along the grain boundaries resulting from precipitation of Cr-rich carbides at the grain boundaries. Whereas, the new mechanism proposed by Kim et al. states that Cr-depletion is due to the segregation of un-reacted Cr atoms around carbides of the stabilizing elements (Ti or Nb) along the grain boundaries, but not due to the formation of Cr-rich carbides [16]. Both mechanisms consider the carbide precipitates (Cr-rich carbides or carbides of the stabilizing elements) along the grain boundaries important, although they have different views on how the different carbides affect the formation of the Cr-depleted zone. In this study, we found that the sensitization and IGC has occurred in the aged steel specimens even without any carbide precipitation along the grain boundaries.

To investigate the distribution of the elements at the grain boundaries of the aged steel specimens, STEM with EDS mapping was further carried out to determine whether there were some fine precipitates (at the nanoscale) to induce the depletion/enrichment of Cr or other elements. Fig. 7 shows the STEM images of the grain boundaries of the specimen aged at 450°C for 200 h and the corresponding EDS element maps of Fe, Cr, C, Mo, and Ni. As can be seen in Fig. 7 (b)-(f), the distributions of Fe, Cr, C, Mo, and Ni at the grain boundaries were almost homogeneous and no

depletion/enrichment of elements was observed, which is not consistent with the typical element maps around the Cr-rich carbides along the grain boundaries [53]. It should, however, be noted that in the EDS mapping, the magnetism of ferritic stainless steel inevitably affects the deflection of the electron beam leading to the drift of the beam and image, which does not result in a high precision and sensitivity of the EDS mapping.

Nevertheless, the nanoscale characterization of the grain boundaries indicates that no precipitation was formed to induce the depletion/enrichment of Cr or other elements. Therefore, another inhomogeneous distribution of Cr responsible for the IGC has to be looked for. Evidence for this hypothesis has been obtained by APT showing that radiation-induced depletion of Cr is observed at the grain boundaries in ferritic stainless steels without the presence of any carbide phases [21-24]. It is also reported that Cr co-segregated with C at the grain boundaries for several atomic layers before carbide nucleation in many aged alloys [36-40]. The real co-segregation layer is less than 1 nm in width, which spreads to a wider region due to the trajectory aberration during the APT when analyzing the interfaces [38, 54]. In the current study, we could not obtain the information of Cr-C co-segregation layer by TEM and STEM because of the magnetic effect of the ferritic stainless steels. However, this does not prevent us from understanding another inhomogeneous distribution of Cr with the help of the co-segregation before carbide nucleation. In the case of low C (0.0064 wt%) and low Cr (11.08 wt%) steel, the Cr co-segregation with C at the grain boundaries before carbide nucleation may induce the formation of Cr-depleted zone responsible for the IGC. The low C content of the investigated steel is not sufficient for the nucleation of carbides

[21, 37]. In addition, the low Cr content is at the edge of the critical value to maintain passivity [6]. Thus, any consumption of Cr by segregation will induce the formation of the Cr-depleted zone at the grain boundaries. The Cr-depletion is distinctly observed when the grain boundaries remain segregated with Cr and C without carbide precipitation [21-24].

The IGC behavior of the investigated steels can be clarified by the Cr-depletion based on the co-segregation of Cr and C before carbide nucleation. Fig. 8 illustrates schematically the comparison of the three mechanisms of IGC. Fig. 8 (a) shows the new IGC mechanism for the investigated steel. With low content of C and Cr, co-segregation of C and Cr before carbide nucleation consumes the Cr atoms around the grain boundaries during aging, which leads to the formation of a Cr-depleted zone contributing to the susceptibility of IGC. Fig. 8 (b) displays the conventional IGC sensitization mechanism for most stainless steels. The precipitation of Cr_{23}C_6 results in the depletion of Cr along the grain boundaries [5, 6, 51, 52] and hence induces the sensitization to IGC. Fig. 8 (c) shows the mechanism proposed by Kim et al. for Ti-stabilized ferritic stainless steels. The Cr-depletion is due to the segregation of unreacted Cr atoms around the carbides of stabilizing elements (Ti or Nb) along the grain boundaries, but not due to the formation of Cr-rich carbides [12, 13, 16].

3.4.2 SKPFM

In order to establish the relationship between the microstructure and the corrosion performance, SKPFM was employed to detect the Volta potential distribution along the

grain boundaries of the investigated steel. It is reported that the materials with the high Volta potential and high work function have higher electrochemical nobility and stability of valence electrons and thus demonstrate better corrosion resistance [55-57]. On the contrary, materials with a lower Volta potential and lower work function are less stable and corrode easier in a galvanic couple [55]. Fig. 9 displays the Volta potential distribution along a grain boundary of the specimen aged at 450°C for 200 h and the corresponding linear Volta potential profiles across the grain boundaries marked as GB₁ and GB₂. As can be seen in Fig. 9 (a), the color of the triple point of grain boundaries is darker than that of the surrounding matrix, which demonstrates that the grain boundaries had a more negative Volta potential than that of the matrix. Fig. 9 (b) shows the remarkable Volta potential difference between the matrix and the grain boundaries, which contributes to the preferential attack of the grain boundaries with a lower Volta potential. The drop of the Volta potential at the grain boundaries originates mainly from the precipitation of a less noble second phase along the grain boundaries [58, 59], the depletion of Cr induced by a noble second phase [49, 60] or depletion induced by segregation related to the transition of alloy chemistry across the grain boundaries [61]. In the current case, the drop of the Volta potential at the grain boundaries is not related to the precipitation of a second phase but related to the depletion of Cr induced by segregation before carbide nucleation, which contributes to the susceptibility to IGC of the investigated steel.

3.4.3 Relationship between microstructure and corrosion performance

The results suggest that the IGC behavior of the studied ferritic stainless steel results from a Cr-depleted zone induced by co-segregation before carbide nucleation. This may provide unique understanding of the relationship between the microstructure of the grain boundaries and the IGC performance. The relationship between microstructure and corrosion performance can be presented as follows.

During the solution treatment at 1300°C, the solute atoms of Cr and C are dissolved in the matrix and grain boundaries homogeneously. Due to the effect of non-equilibrium grain boundary segregation [62] during the subsequent water quenching, a slight Cr-depleted zone is formed but cannot be observed using the conventional TEM [63], which contributes to the slight corrosion at the grain boundaries in the form of small sporadically distributed pits (Fig. 2 (a)). The homogeneous matrix is covered by a protective passive film and thus nearly uncorroded.

When the samples are aged at 450°C for 2 h, the solute C atoms begin to segregate to the grain boundaries from the surrounding matrix due to the equilibrium grain boundary segregation [64]. On one hand, the atoms of Cr segregate with C to the grain boundaries [37-40] due to the effect of co-segregation [64, 65]. As discussed in Fig. 8 (a), the Cr-depleted zone is induced by the co-segregation before carbide nucleation, which leads to IGC. Moreover, the localized IGC in the form of a corrosion ditch distributed discontinuously along the grain boundaries (Fig. 2 (b)) may relate to the periodic variation of the segregation along the grain boundaries due to the free volume distributed discontinuously at the grain boundary plane depending on the misorientation between the two neighboring grains [37]. On the other hand, the Cr atoms preferentially

segregate at dislocations and matrix defects [66, 67] in the grain interior and inevitably form the Cr-depleted zones in the matrix responsible for the slight pitting corrosion attack (Fig. 2 (b)).

For the samples aged at 450°C for 20 h, more Cr atoms segregate to the grain boundaries and the dislocations and matrix defects in the grain interior. The discontinuous segregation zones gradually grow and interconnect with the adjacent segregation zones, which may relate to the formation of semi-continuous Cr-depleted zones contributing to the semi-continuous IGC (Fig. 2 (c)). In addition, the segregation around the dislocations and matrix defects in the grain interior may result in Cr-rich clusters observed around matrix defects by APT [66], which may lead to a severe Cr-depletion in the matrix responsible for the pitting corrosion attack distributed densely over the surface (Fig. 2 (c)).

When aged for 200 h, the semi-continuous segregation zones of Cr tend to interconnect further with the adjacent segregation zones to form the continuous segregation. This can induce the continuous Cr-depleted zone acting as the micro-anode [63] responsible for the continuous IGC with the corrosion ditch formation along the grain boundaries (Fig. 2 (d)). Meanwhile, the dislocations and the matrix defects migrate to the grain boundaries due to the recovery processes, which leads to a decrease in the local enrichment of Cr in the matrix and, thus, no pitting corrosion attack occurred in the matrix. However, the matrix underwent slight general corrosion (Fig. 2 (d)) induced by the lower bulk Cr content [41] resulting from the strong Cr-enrichment at the grain boundaries.

This study therefore expands the understanding of the relationship between the microstructure of the grain boundaries and the IGC performance as compared to the existing conventional sensitization mechanism [5, 6, 51, 52] and the mechanism proposed by Kim et al. [12, 13, 16]. Most notably, this is the first study to our knowledge to investigate the behavior of IGC before carbide nucleation. Our results provide compelling evidence for the susceptibility to IGC without carbide formation and indicate that this new mechanism of IGC may establish the theoretical foundation for developing a new method or new steel to prevent IGC. These results may also have implications on the basic mechanism and the prevention of IGC happening in the nuclear materials due to the radiation-induced segregation and Cr-depletion at the grain boundaries.

Although our results support the susceptibility to IGC without carbide precipitation and the hypothesis was established based on the results and the literature, the direct evidence for the Cr-depletion induced by co-segregation is lacking. Future work should therefore include the analysis of the Cr-depleted zone induced by C-Cr co-segregation at the grain boundaries using the instruments with very high spatial resolution.

4. Conclusions

We have demonstrated that the investigated ferritic stainless steel with low Cr content is susceptible to intergranular corrosion without any carbide precipitation after aging. The intergranular corrosion susceptibility of the aged steel can be attributed to the Cr-depleted zone induced by Cr-C co-segregation before carbide nucleation, which

is significantly different from the the existing conventional sensitization mechanism and the mechanism proposed by Kim et al.

The intergranular corrosion susceptibility of the aged steel increases with increasing aging time. The intergranular corrosion morphology changes from discontinuous (aged for 2 h) to semi-continuous (aged for 20 h) and to continuous (aged for 200 h), which can be attributed to the transitions of the Cr-depleted zone induced by co-segregation with increasing aging time.

Author statement

Shuai Hu: Conceptualization, Methodology, Investigation, Data Curation, Writing – Original Draft. **Yaozong Mao:** Validation, Resources. **Xianbin Liu:** Supervision, Funding acquisition. **En-Hou Han:** Project administration. **Hannu Hänninen:** Writing- Reviewing and Editing

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Fig. 1. Microstructures of the grain boundaries (GBs) of specimens aged at 450°C for: (a) 0 h, (b) 2 h, (c) 20 h, and (d) 200 h.

Fig. 2. Intergranular corrosion (IGC) morphology of specimens aged at 450°C for (a) 0 h, (b) 2 h, (c) 20 h, (d) 200 h and (e) the relationship between the IGC rate and aging time.

Fig. 3. DL-EPR curves of specimens aged at 450°C for 0 h, 2 h, 20 h, and 200 h.

Fig. 4. Corrosion morphology of the aged specimens after potentiostatic polarization at E_{+r2} or E_{+r3} : (a) 2 h - E_{+r2} , (b) 20 h - E_{+r2} , (c) 20 h - E_{+r3} , (d) 200 h - E_{+r3} .

Fig. 5. Relationship between the values of DOS and aging time.

Fig. 6. TEM images of grain boundaries of specimens aged at 450°C for (a) 0 h, (b) 2 h, (c) 20 h, (d) 200 h.

Fig. 7. STEM images of grain boundaries of specimens aged at 450°C for 200 h and corresponding EDS element maps of (b) Fe, (c) Cr, (d) C, (e) Mo, (f) Ni.

Fig. 8. Schematic illustration of the differences between the three mechanisms of IGC: (a) current study: Cr-depletion induced by co-segregation, (b) conventional sensitization mechanism: Cr-depletion induced by Cr_{23}C_6 precipitation, (c) Kim et al.'s mechanism: Cr-depletion induced by segregation around carbides of stabilizing elements (Ti and Nb).

Fig. 9. (a) Volta potential distribution at grain boundaries of specimen aged at 450°C for 200 h, and (b) linear Volta potential profiles across grain boundaries GB₁ and GB₂.

Wt.%	Cr	C	N	Mn	Mo	Si	Ni	Fe
Alloy	11.08	0.0064	0.0042	0.4	0.81	0.46	1.8	Bal.

Table 1 Chemical composition of the low-Cr ferritic stainless steel.