The Effect of Solution Treatment on Intergranular Corrosion Resistance of a New Type Ultra Low Carbon Stainless Steel

Wang Julin[1], Ni Nannan[1], [†] Yan Qingling[2], and Liu Lingli[2]

[1]*Beijing University of Chemical Technology, Beijing 100029, china*
[2]*R&D Center of PetroChina Pipeline Company, Langfang 065000, china*

In the paper, with corrosion velocity measurement and metallographic observation on specimens after sulfuric acid/ferric sulfate boiling experiment, intergranular corrosion tendency of the new type ultra low carbon stainless steel developed by ourselves which experienced solution treatment at different temperatures was evaluated. A VHX 500 super depth field tridimensional microscope was used to observe corrosion patterns on the sample surfaces. The depth and width of grain boundary corrosion groove were measured by the tridimensional microscope, which indicated that the corrosion degrees of the samples which received solution treatment at different temperatures are quite different. Transgranular corrosion at different degree occurred along with forged glide lines. After comparison it was proved that the stainless steel treated at 1100 ℃ performs very well against intergranular corrosion.

Keywords *: new ultra low carbon stainless steel, intergranular corrosion, metallographic morphology, solid solution treatment*

1. Introduction

During the smelting, welding or heat treatment of metals and alloy, compounds which contain impurities such as C, P and Si etc., and precipitated phase inevitably shall be separated out at grain boundary. Therefore, intergranulars are preferentially to be oxidized, vulcanized or hydrogenised, resulting to intergranular corrosion.[1] So called as intergranular corrosion, with poverty of metal element in alloys in specific media or at high temperature, local corrosion occurs along grain boundary, and binding force between grains is lost.[2] This corrosion type which develops into the substrate is invisible on surface, but its reticular structure can be observed with metallographic microscope.

As an important process of metallic material manufacturing, solution treatment is largely used to achieve even austenite structure, increase corrosion resistance, eliminate work-hardening and soften the steel to ensure easy shaped.[3] Additionally, re-solution treatment is the most effective method to prevent intergranular corrosion and precipitation of σ-phase (intermetallic compound of FeC). When stainless steel was heated above solubility

curve (σ-phase disappears above 850 ℃) and kept insulating for a period, the $Cr_{23}C_6$ can be sufficiently dissolved, dispersed and distributed uniformly, then oversaturated austenite structure can be achieved by quick cooling without the $Cr_{23}C_6$ separation out. Generally, solution treatment temperature of austenite is from 1050 ℃ to 1150 ℃. The higher content of carbon, the higher solution treatment temperature is needed.[4] The samples used in the experiment are made of the new type ultra-low-carbon stainless steel which was solution treated at different temperatures. It was essential to investigate the effect of solution treatment on intergranular corrosion resistance of the stainless steel and establish the best solution treatment temperature.

So far, many methods are being used to assess intergranular corrosion of stainless steel. Different methods were suitable for different kinds of stainless steels. Wu Jinhua,[5] Beuhler[6] used electrochemical potentiodynamic reactivation (EPR) method to measure the susceptivity of intergranular corrosion and considered the method as an accurate, prompt and ideal one till now. By added NaCl to standard solution of DLEPR and enlarged the concentration of H_2SO_4, Lopez detected the effect of σ-phase on intergranular corrosion resistance of austenite stainless steels and perplex stainless steels.[7,8] Zhang Wei etc. studied the susceptivity of intergranular corrosion of 304L us-

[†] Corresponding author: Julinwang@126.com

ing constant potential erosion method. The result indicated that constant potential erosion may be developed into a prompt test method in this field.[9] Using constant current erosion of stainless steel in 10% oxalic acid, Na Shunsang and Tian Wei carried out comparison tests among various electrolytic parameters, and revealed that both electrolytic current and time are main factors to the degree of intergranular corrosion.[10] However, 10% ammonium persulfate, not 10% oxalic acid, can be used in electrolytic etching of stainless steel which contains molybdenum.[11),12)] Besides electrochemistry method, chemical erosion of the stainless steel in solutions such as 65% nitric acid, sulfuric acid/cupric sulfate, nitric acid/hydrofluoric acid can also be done on this purpose, after erosion metallographic observation, flexural measurement, weight loss, sonic ranging and ultrasonic thickness measurement were used to assess intergranular corrosion of the stainless steel. Jean-Pierre Celis found intergranular corrosion is induced after a single step pickling in HF electrolyte while not in HCl and the depth of intergranular corrosion obtained from a multi-step pickling is dependent on the successive sequence and duration of the two electrolytes used.[13] Fanny Balbaud found corrosion of stainless steels in the nitric acid condensates is far more severe than in the liquid bulk and can lead to intergranular attack even on non-sensitized steels.[14] Wheeler applied ultrasonic testing to measure stainless-steel pipelines in the coolant water system of Savannah River Site (SRS) reactors, and the results indicated the presence of short, partly through-wall stress corrosion cracks in the heat-affected zone of approximately 7% of the circumferential pipe welds. These cracks were thought to be developed by intergranular nucleation and mixed mode propagation.[15]

According to the composition of the new type ultra-low-carbon stainless steels, sulfuric acid/ferric sulfate immersion experiment conjunction with weight loss and metallographic observation, intergranular corrosion tendency which experienced solution treatment at different temperatures was evaluated. As a double-reagent method, the ferric sulfate was used as passivating agent in sulfuric acid/ferric sulfate system. The method is chiefly used to test intergranular corrosion of austenitic stainless steels containing molybdenum, and intergranular corrosion caused by chromium carbides in un-stabilized austenitic stainless steel (such as 316L, 317L), and also intergranular corrosion caused by both chromium carbides and σ-phase in stabilized austenitic stainless steel (such as 321 etc.) Although 65% nitric acid was also usually applied to test the intergranular corrosion caused by σ-phase, it was often accompanied by severe general corrosion and thus not suitable in the tests.

2. Experimental

2.1 Chemical composition of the new developed stainless steel and solution treatment temperatures

The composition of samples 1, 2, 3, and 4 was the same as Table 1 and the solid solution temperatures were described in Table 2.

Table 1. Chemical composition of samples (mass weight %)

C	Si	Mn	S	P	Cr	Ni	Mo	N	O	Fe
0.002	0.25	0.48	0.003	⟨0.005	17.60	15.30	2.55	0.0025	0.0024	rest

Table 2. Solution treatment temperature (℃)

No.	solution treatment temperature
1	Without treatment
2	900
3	1000
4	1100

Remark: Solid solution treatment duration was two hours.

2.2 Sulfuric acid/iron sulfate immersion test (GB/T4334.1-2000)

2.2.1 Test solution

Mixing sulfuric acid (GR) with distilled water of the same weight. Put 12.5 g of iron sulfate into 300 ml of the solution and heat the solution till complete dissolution.

2.2.2 Test apparatus and equipment

(1) 500 ml ground glass stoppered conical flasks with condensation reflux pipes were used as experimental containers;
(2) A set of heating facility which can keep the solution slightly boiling;
(3) A square calliper was used to measure the superficial area of the samples;
(4) A set of electronic balance was used for samples weight measurement.

2.2.3 Test procedure

(1) Measuring the sizes of samples and calculating their superficial areas;
(2) Weighing samples before the test;
(3) The quantity of solution was determined by the superficial area of samples, which should not be less than 20 ml/cm^2. The solution must be new prepared for each test;
(4) Samples were positioned at the middle of the solution with a glass support. Keep boiling for 120 hours;
(5) Took out the samples after test. Scrubbed off corrosion product from samples in running water with

soft brush, then rinsed the samples with distilled water and weighed them.

2.3 Test of corrosion rate and observation of the corrosion patterns on samples surface

After erosion in sulfuric acid/ferric sulfate the samples were taken out and scrubbed off corrosion product in running water with soft brush, then rinsed with distilled water and surveyed the corrosion rate by weight loss. An Axioplan2 universal material microscope (Zeiss company, Germany) was used to observe corrosion patterns on the sample surface and assess intergranular corrosion class, while a VHX-500 super-deep focus tridimensional microscope (Keyence company) was used to the observe tridimensional corrosion patterns on sample surface and measure depth and width of grain boundary corrosion channels.

3. Results

According to GB/T4334.1-2000, the weight loss of stain-

Table 3. General corrosion rates of stainless steel samples experienced sulfuric acid/iron sulfate erosion test

Samples	1	2	3	4
general corrosion rate $(g/m^2.h)$	0.64	0.71	0.60	0.40

less steel samples which experienced 120 hours sulfuric acid/ferric sulfate erosion test is used to calculate the general corrosion rate $(g/m^2.h)$. The results are shown in Table 3.

The increasing sequence of the general corrosion rates of stainless steel samples is 4, 3, 1, 2.

Fig. 1 is metallograph morphology of the new type super-low-carbon stainless steels which had been treated at different temperatures in sulfuric acid/ferric sulfate solution. From Fig. 1, it can be seen that the new type super-low-carbon stainless steels which had been treated at different temperatures are all subjected to intergranular corrosion at different degrees, grain-boundary corrosion ditches are obvious on each sample surface. The most severe one among them is No. 2 sample, which has wide
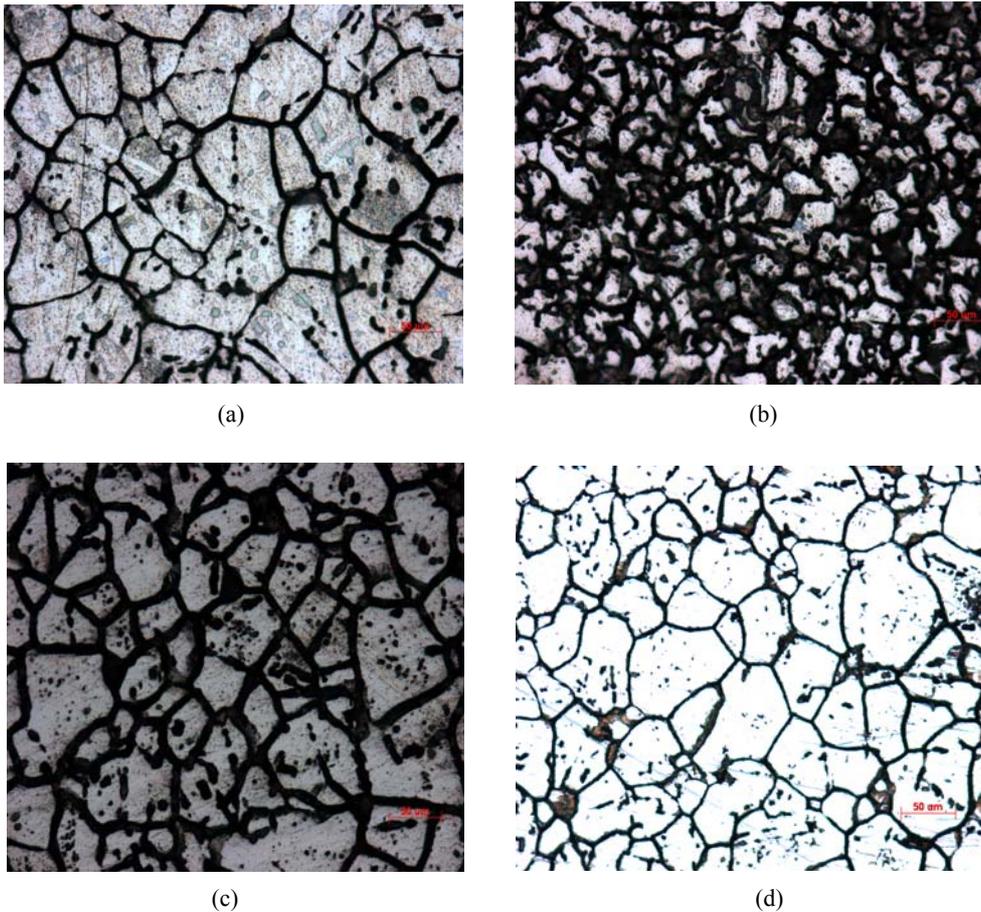

(a)

(b)

(c)

(d)

Fig. 1. Metallograph of the new type super-low-carbon stainless steels which has been treated at different temperatures in sulfuric acid/ferric sulfate solution

and deep grain-boundary corrosion ditches, in addition with some grains pulled off. Sample 3 is less corroded, and the grain-boundary is consecutive with no grains pulled off. Some grain-boundary corrosion ditches on No.1 sample are comparatively obvious, while some grain-boundary is not consecutive. Corrosion status on it is remarkably slighter than sample 2 and 3. Grain-boundary corrosion ditches on No. 4 sample are narrow and shallow.

Some grain-boundary is not consecutive. Intergranular corrosion resistance is prominently the best. The increasing sequence of intergranular corrosion resistance of the new type ultra-low-carbon stainless steels is 4, 1, 3, 2, which conforms to the result of weight loss.

Fig. 2 is a tridimensional pattern view of the new type ultra-low-carbon stainless steels experienced treatment at different temperatures subject to sulfuric acid/iron sulfate
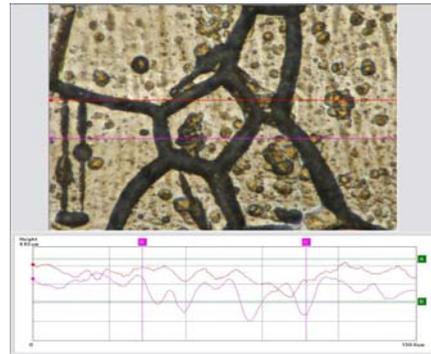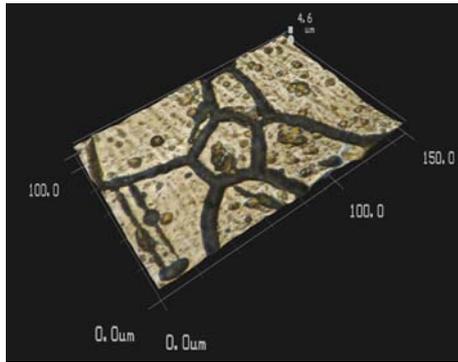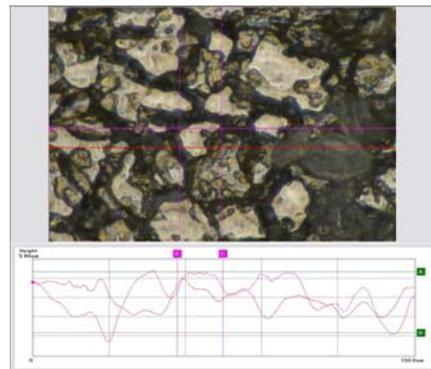

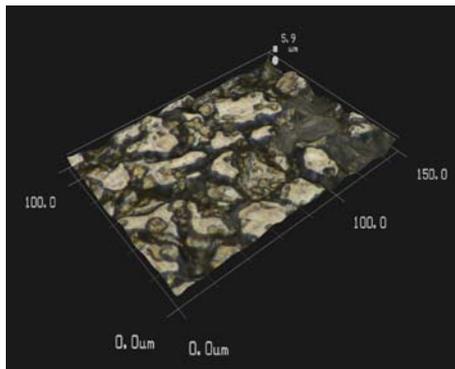**Fig. 2.** (a) No.1 (without solid solution treatment)

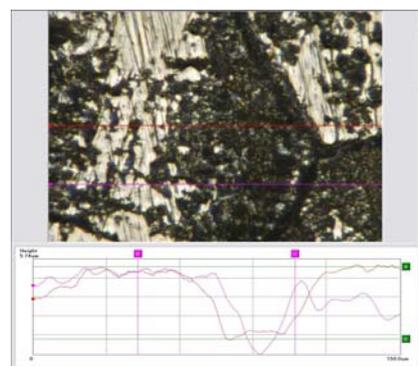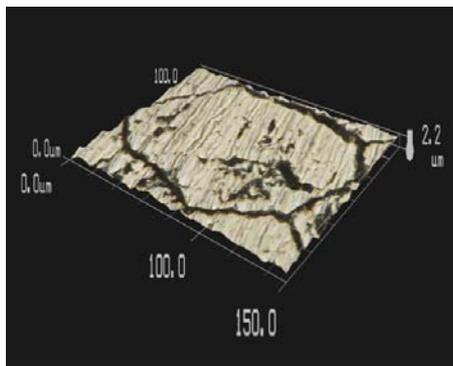**Fig. 2.** (b) No. 2 (solid solution treatment at 900 ℃)

Fig. 2. (c) No. 4 (solid solution treatment at 1100 ℃)

Fig. 2. Tridimensional pattern view of the new type ultra-low- carbon stainless steels experienced treatment at different temperatures subject to sulfuric acid/iron sulfate erosion test

erosion test. It reveals ulteriorly the large difference of intergranular corrosion status of them. In Fig. 2, the maximum depth of grain-boundary corrosion ditches on No. 1 sample (without solid solution treatment) is 4.6 µm, and grains separate from each other. A little corrosion occurs in grains. As for No. 2 sample, grains have been fragmentaryly corroded. Grain boundary corrosion ditch on No. 2 sample is 5.9 µm deep. Because of severe abscission of grains, height curve of surface does not wave severely. Grain boundary corrosion ditch on No. 4 sample is only 2.2 µm deep. It can also be found in Fig. 2 that the new type super-low-carbon stainless steels which both experienced treatment at different temperatures or without treatment not only corrode on grain boundary, but also on the grains at different degrees. Making No. 4 sample as an example, Fig. 2(c) is a tridimensional pattern view of a whole grain of the new type super-low-carbon stainless steel which experienced treatment at 1100 ℃ and then suffered sulfuric acid/iron sulfate erosion test. In Fig. 2(c), grains completely protrude. Corrosion appears not only on the grain-boundary, but also in grains as black corrosion region. After measuring the height of grains layer, it is found that the black corrosion region is deeper than surface around and is sunk. Shown as Fig. 3, these ribbons exactly position along with forged glide lines. In order to improve the resistance of austenitic stainless steel against intergranular corrosion, it is discovered that proper cold-working (such as forging) can be helpful to change the core forming position of carbon compound, and impell precipitation phase to separate out along with glide lines in grains and reduce the amount of grain-boundary precipitation.[17] Therefore, both No. 1 and 4 samples with relative higher resistance to intergranular corrosion are corroded along with forged glide lines.

4 Discussions

There were much mechanism causing intergranular corrosion, general thinking was the poverty of alloy elements on grain boundary, in other words, electrochemical non-uniformity caused by poverty of chrome in solid solution which connect edges of the grains. If austenitic stainless steel was kept at temperature from 450 ℃ to 850 ℃ for enough duration, carbon existed at edges of grains would firstly react with chrome which was contained in Fe-Cr-Ni solid solution at the brim of grains to form $Cr_{23}C_6$ (because chrome tended to form carbide than iron and nickel). $Cr_{23}C_6$ precipitated at the grain-boundary of austenite resulted in decreasing of chrome concentration in solid solution which located among grains. With the reducing of content of chrome in solid solution, its elec-

Sample 1

sample 4

Fig. 3. Photographs of ribbon-like corrosion along forged lines on No. 1 and 4 samples

trode potential changed correspondingly. If the mass percent of chrome in solid solution near edges of grains was lower than 12%, the area became to an active region in many kinds of electrolytes. In galvanic couple which was formed with chrome poverty area as its anode and normal chrome content solid solution as its cathode, small anode region and large negative zone made the active region subject to consuming corrosion and damage.[18] Within certain scope of solid solution temperatures, with increasing of the temperature, both dissolvability of carbon and nitrogen in austenite and diffusion velocity of the elements were speeded up, the grain boundary absent of chrome was not easy to form. In this case, although $Cr_{23}C_6$ started precipitating for a long time, it did not bring materials the tendency of intergranular corrosion. In the contrary, decreasing temperature might slower diffusion velocity of the elements and quicken precipitated speed of $Cr_{23}C_6$, therefore chrome compensated for grain boundary is not enough to balance the consumption. Once if the content of chrome reduced to certain level, materials would tend to intergranular corrosion.[19] Maysa Terada pointed that the solution-annealed samples and those aged at 1173 K did not present susceptibility to intergranular corrosion,

whereas aging treatment from 873 to 1073 K resulted in small susceptibility to intergranular attack that decreased with aging temperature increase. The preferential formation of MoC at higher aging temperatures comparatively to $Cr_{23}C_6$, retained the chromium in solid solution reducing susceptibility of steel to intergranular corrosion.[20] But it needed to be noticed that with decrease of carbon in stainless steel, precipitation of $Cr_{23}C_6$ reduced correspondingly at the grain-boundary, both chances of forming regions absent of chrome and the tendency of intergranular corrosion were reduced. Korostelev showed that there was a maximum permissible carbon content level, below which stainless steel would not subject to intergranular corrosion.[21] Austenitic stainless steels are classified into three grades according to the content of carbon: general amount of carbon (Wc<0.14%), low carbon class (Wc<0.06%) and ultra-low-carbon class (Wc<0.03%). Because the maximum mass percent of carbon dissolved in austenite can be 0.02%-0.03% at room temperature, in principle, intergranular corrosion would not occur in ultra-low-carbon austenitic stainless steels if their chemistry composition was qualified. But such resistant to intergranular was not absolute, under certain conditions, such as with the existence of strong oxidizing agent, intergranular corrosion can also occur.[22]

In many cases, intergranular corrosion occurred in ultra-low-carbon austenitic stainless steels was caused by precipitation of another high chrome content phase along the edges of grains. The first was σ-phase or submicroscopic α-phase, which resulted in absence of chrome at grain-boundary. Additionally, because σ-phase was more resistant to corrosion than γ-phase (the phase composed of solid solution), the region lack of chrome will be corroded under strong oxidation reduction potential.[23] Secondly, segregation of impurity at grain-boundary can also resulted in severe intergranular corrosion in super-low-carbon austenitic stainless steels. The theory was put forward aiming to intergranular corrosion of stainless steels in strong oxidizing medium. It was considered that in this case, selective solution of impurity (such as P and Si) which segregated at grain-boundarywas the main reason of intergranular corrosion in stainless steels.[24] The effect of Si on tendency of intergranular corrosion of stainless steels was complicated. Someone thought that corrosion resistance of passivating film containing Si is better than those without Si because of passivation function of Si. However, if high Si passivating films was formed only on grains surface, at meanwhile the same corrosion resistant film can not be achieved at grain-boundary, difference between two kinds of films will result in intergranular corrosion. When mass percent of Si was more than 4%

or less than 0.1%, intergranular corrosion would not tend to occur in the stainless steel. Another theory in view of grain-boundary energy considered that deficiency of Si is easier to lead to segregation of impurity on grain-boundary, which made the grain-boundary have comparative high energy resulting in intergranular corrosion.[25] Other studies indicated that the content of impurity phosphorus absorbed at grain-boundary is related with solid solution temperature and the corrosion degree at grain-boundary increase rapidly with the content increment of phosphorus.[26] Concern of the composition of the ultra-low-carbon stainless steels in this experiment, there are infinitesimal carbon and certain amount of Si and P. The relative severe intergranular corrosion occurs in samples which experienced solution treatment at 900 ℃ and 1000 ℃ may be caused by aliquation of impurity (Si and P) on grain-boundary, or by the precipitation of σ-phase.

The new ultra low carbon stainless steels in the experiment contain certain amount of Si and P. After solution treatment at different temperatures, the adsorption difference between phosphorus and Si at grain-boundary leads to different resistance to intergranular corrosion.

Mentioned as above, solid-treatment temperatures influenced intergranular corrosion of stainless steel through influencing dissolvability, diffusion velocity of some elements in it, or precipitation and dissolution velocity, position and phase change of deposit phase. Shimada discovered slight pre-strain annealing at a relatively low temperature can result in excellent intergranular corrosion resistance due to optimized grain boundary character distribution (GBCD), i.e. the uniform distribution of a high frequency of coincidence site lattice boundaries and consequent discontinuity of random boundary network in the material.[27]

In the experiment, the new type super-low-carbon stainless steel experienced treatment at 1100 ℃ performs obviously better resistance to intergranular corrosion. On the contrary, resistance to intergranular corrosion of the steel which experienced treatment at 900 ℃ and 1000 ℃ are worse than No. 1 sample which had not been treated at all. This indicates that solution treatment technology can weaken or erase tendency of intergranular corrosion of alloys in some cases, and can also accelerate it in other cease. Therefore, it is necessary to carry out test for best solution treatment temperature and excellent resistance to intergranular corrosion.

5. Conclusions

Both sulfuric acid/ferric sulfate weight loss analysis and metallographic observation indicates that the newly devel-

oped super-low-carbon stainless steel which experienced treatment at 1100 ℃ performs obviously better resistance to intergranular corrosion. On the contrary, resistance to intergranular corrosion of the steel treated at 900 ℃ and 1000 ℃ are worse than No. 1 sample which had not been treated.

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