Corrosion Behavior Research on Austenitic stainless steel in Dynamic Molten Salt

Pengcheng Che\textsuperscript{1,3, a}\textsuperscript{*}, Fengjun Wang\textsuperscript{1, b}, Min Xie\textsuperscript{1, c}, Qi Li\textsuperscript{2, d}, Zhang yikun\textsuperscript{2, e}, Yi Cheng\textsuperscript{2, f}

\textsuperscript{1}Harbin-electric power generation equipment national engineering research center CO., LTD., Harbin, 150028, China
\textsuperscript{2}State Key Laboratory of Efficient and Clean Coal-Fired Utility Boilers, Harbin Boiler Company Limited, Harbin, 150046, China
\textsuperscript{3}Harbin Institute of Technology, Harbin, 150000, China
\textsuperscript{*}Corresponding author: \textsuperscript{a}email: chepc@harbin-electric.com.
\textsuperscript{b}email: hit18045370688@163.com, \textsuperscript{c}email: xiemin@harbin-electric.com.
\textsuperscript{d}email: liqi@hbc.com.cn, \textsuperscript{e}email: zhangyk@hbc.com.cn.
\textsuperscript{f}email: chengyi@hbc.com.cn.

Abstract: In order to identify the corrosion properties of three kinds of austenitic stainless steel used in solar power plant, experiments were conducted to test the weight loss after dynamic immersing in molten salt, the corrosion thickness rates per year was obtained, and the surface morphology by SEM and component of corrosive product by EDS were analyzed. The test result showed that the corrosion resistance of 316L and 347H are outstanding, much better than 304. The corrosion resistance order of the three material is 304 < 316L < 347H. 304 and 316L can be considered as the candidate materials of low-temperature molten salt storage tank, and 347H can be used as the materials of high-temperature molten salt storage tank and molten salt heat exchanger.

1. Instruction
How to reduce haze and make clean and efficient use of energy has always been an important topic studied by experts at home and abroad. Solar thermal power generation technology uses sunlight as the energy source, which is green and sustainable, attracted more and more attention \cite{1}. Since molten salt can be used as heat transfer medium to realize the integration of heat absorption, heat transfer and heat storage, and supply stable electric energy to the power grid, the molten salt solar thermal power generation technology has developed rapidly, and many commercial projects have been put into construction all over the world \cite{2}.

In the heat storage and exchange system, a large number of metal materials need to be used in the heat storage tank, heat exchanger and heat transfer pipeline. When molten salt flows as heat transfer medium, it will cause serious corrosion, finally lead to failure like thinning and cracking of heat exchanger pipes, leakage of molten salt and so on. There are few reports on the dynamic corrosion of molten salt on metal materials in heat storage and exchange system. Therefore, the research on the dynamic and static corrosion performance of molten salt to metal materials in high temperature is of great significance to guide the design of molten salt heat absorber and material selection.
2. Test materials and molten salt medium

Austenitic stainless steel 304, 316L and 347H are commonly used corrosion resistance material as molten salt pipes. In order to study the corrosion characteristics of the three materials by high-temperature molten salt, the three grades were selected and tube samples were taken, the corrosive medium is dualistic molten salt system: 60% NaNO₃ - 40% KNO₃. The chemical composition of the three materials are shown in Table 1 [3].

| Metal | C   | Si  | Mn  | P   | S   | Cr  | Nb+V+Ti | Mo | Ni | Cu | Fe |
|-------|-----|-----|-----|-----|-----|-----|---------|----|----|----|----|
| 304   | 0.04| 0.51| 1.06| 0.02| 0.005| 18.43| -       | -  | 8.04| -  | -  |
| 316L  | 0.038| 0.472| 1.284| 0.02| 0.0019| 16.84| -       | 2.08| 10.12| 0.09| -  |
| 347H  | 0.04| 0.55| 1.18| 0.02| 0.001| 17.19| 0.49    | -  | 9.23| -  | -  |

3. Kinetics experiment of molten salt hot corrosion

3.1 Experimental objectives

As the 304, 316L and 347H stainless steel are selected as candidate materials of molten salt heat absorber, their dynamic corrosion mechanism by 570°C/60% NaNO₃ - 40% KNO₃ molten salt were studied. The thermal corrosion kinetics experiment was mainly to obtain the annual corrosion rate and annual corrosion thickness. Through comparing the corrosion characteristics of three metal materials in molten salt, so as to provide a guidance for the material selection and design scheme of molten salt storage tank and molten salt heat exchanger.

3.2 Experimental scheme

3.2.1 Dynamic corrosion

1) Sample pretreatment: cut the tube samples (304, 316L and 347H) to 30×20×3mm sheet sample, perforated in the middle part with a hole diameter of 5mm, polished and ultrasonically cleaned with alcohol for 10 minutes.

2) Fixed the sample on the rotary disk of the dynamic corrosion instrument, then immersed in the molten salt, open the rotary table to a specified speed of 200r/min (the flow rate of simulated molten salt is 2.5m/s), maintained the molten salt temperature at 570°C.

3) After soaking for 50h, 100h, 500h, 1000h and 15000h respectively, take a sample at each corrosion time condition, clean the corrosion products according to GB/T 16545-1996, weighed the sample mass, and then calculated the weight loss rate, annual corrosion rate and annual corrosion thickness.

3.2.2 Corrosion rate calculation

According to the formulas of corrosion rate calculation 1-1, 1-2 and 1-3 [4]:

\[ V_1 = \frac{k_1(M_2 - M_1)}{S} \]  (1-1)

\[ V_2 = \frac{k_2(M_2 - M_1)}{ST} \]  (1-2)

\[ V_3 = \frac{k_3(M_2 - M_1)}{STD} \]  (1-3)

Where, \( V_1 \) represents weight loss, Unit: g / mm²

\( V_2 \) represents annual corrosion rate, Unit: g / mm² / a

\( V_3 \) represents annual corrosion rate, Unit: mm / a

\( k_1, k_2, k_3 \) are constants, \( k_1 = 1 \), \( k_2 = 8760 \), \( k_3 = 8.76 \times 10^6 \)

\( M_1 \) represents sample mass after experiment, Unit: g

\( M_2 \) represents sample mass before experiment, Unit: g

\( S \) represents sample surface area, Unit: mm²

\( T \) represents soaking time, Unit: h
D represents material density, Unit: g/cm\(^3\)

### 3.2.3 Sample morphology characterization

1) Microscopic morphology observation

The micro morphology of corrosion products on the sample surface was observed by scanning electron microscope (SEM).

2) Corrosion product analysis

X-ray energy spectrometer was used to analyze the corrosion products on the sample surface, in order to conform the composition of the corrosion products.

### 4. Analysis and test results of dynamic corrosion

As shown in Fig.1-fig.3, under the dynamic corrosion environment of 570°C and flow rate of 2.5m/s at different corrosion time of 50h, 100h, 500h, 1000h and 1500h respectively, the trend of weight loss rate, annual corrosion rate and annual corrosion thickness were analyzed. It can be seen from the figure that the weight loss rate increases with the increasing corrosion time, oppositely, the annual corrosion rate and annual corrosion thickness decreases. After dynamic immersion in molten salt for 1000h, the difference of weight loss rate between 316L and 347H is not obvious, indicating that the corrosion resistance of the two in molten salt is similar, while 304 has the worst corrosion resistance among the three materials.

![Fig.1 Weight loss rate](image1)

![Fig.2 Annual corrosion rate](image2)

![Fig.3 Annual corrosion thickness](image3)

The annual corrosion thicknesses of 304, 316L, and 347H after 1000h corrosion time are 0.0507mm/yr, 0.025mm/yr and 0.021mm/yr respectively. According to the standard of Mechanical Engineering Material Test Manual (Corrosion and Tribology Volume) in Table 2, corrosion resistance of different metals can be divided into 10 grades, 304 belongs to grade 5, 316L and 347H belongs to grade 4, they are all belong to corrosion resisting steel.

| Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-------|---|---|---|---|---|---|---|---|---|----|
| Corrosion rate (mm/yr) | <0.001 | 0.001~ | 0.005~ | 0.01~ | 0.05~ | 0.1~ | 0.5~ | 1.0~ | 5.0~ | >10.0 |

Table 3 shows the surface morphology of the three materials after immersion in molten salt system for 300h, 500h and 1000h. It can be seen that the sample surface has an obvious uniform corrosion, and a mass...
of loose corrosion products adhered to the surface. The corrosion products of 316L have fallen off, and color of the surface changed from deep to light with time, indicating that composition of the corrosion products had changed.

Table 3 Micro morphology after different corrosion time

|        | 300h | 500h | 1000h |
|--------|------|------|-------|
| 304 stainless steel | ![Image] | ![Image] | ![Image] |
| 316L stainless steel | ![Image] | ![Image] | ![Image] |
| 347H stainless steel | ![Image] | ![Image] | ![Image] |

Table 4 shows the EDS analysis results of the three materials after soaking for different times. The corrosion products on the surfaces of the three samples are mainly iron oxides. At the same time, Cl also existed in corrosion product layer, it is highly corrosive and can permeate into the matrix to form a gap, which led to the structure loose and porous, finally caused the corrosion products falling off. It is the immediate reason for gradually increasing weight loss rate with test time. In addition, Si element also existed in corrosion product layer, it is an error element, which may be caused by the material in the crucible sticking to the sample surface at high temperature.

Table 4 EDS analysis after different corrosion time

|        | 300h | 500h | 1000h |
|--------|------|------|-------|
| 304 stainless steel | ![Image] | ![Image] | ![Image] |
5. Conclusion
In the dynamic corrosion environment, weight loss rate of austenitic stainless steel increases with time, and annual corrosion rate and annual corrosion thickness decrease with time. The corrosion resistance of the 316L and 347H in dualistic molten salt system: 60%NaNO$_3$-40% KNO$_3$ is similar, while the corrosion resistance of 304 is the worst among the three. The order of corrosion resistance is $304 < 316L < 347H$. The corrosion resistance grade of 304 is grade 5 and the grade of 316L and 347H both are grade 4. According to the operation conditions of molten salt storage tank and heat exchanger in solar thermal power generation, 304 and 316L can be considered as the candidate materials of low-temperature molten salt storage tank, and 347H can be used as the materials of high-temperature molten salt storage tank and molten salt heat exchanger.

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