# Development of GH3535 Alloy for Thorium Molten Salt Reactor

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**Abstract** The GH3535 seamless pipe was developed by hot extrusion and cold rolling. The mechanical properties and corrosion resistance of GH3535 seamless pipe under molten salt environment were tested at different temperatures. The results showed that the extrudability of GH3535 alloy was fine at 1150–1250 °C, and the mechanical properties of hot-extruded GH3535 alloy pipe were excellent and the microstructure was uniform. The average grain size of GH3535 seamless pipe is about 67 μm. The yield strength of GH3535 alloy pipe is above 200 MPa at 650–700 °C, the tensile strength is above 480 MPa. The corrosion resistance of GH3535 alloy seamless pipe is also good in high temperature (700 °C) molten salt environment.

**Keywords** Thorium-based molten salt reactor · GH3535 alloy
Seamless pipe · Hot extrusion · Nickel-based

## Introduction

Thorium molten salt reactor (TMSR for shot) is the ideal reactor type with thorium uranium fuel cycle which is included in the candidate fourth-generation advanced nuclear reactor [1, 2]. The major characteristic of the TMSR is the use of molten salt fuel and thorium 232 as raw material for proliferation [3–5]. However, it is very critical to select materials of the pipes, core cladding and structural components of

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the selection in TMSR system due to the corrosive environment of molten salt (650–850 °C).

Ni–Mo–Cr–based Hastelloy N alloy (GH3535) was listed as the candidate material of TMSR [6–8] in the “Advanced Nuclear Fission Energy” of the Chinese Academy of Sciences, which was launched in 2011 by the Chinese Academy of Sciences.

GH3535 alloy with FCC structure is a Ni–Cr–Mo superalloy by solution strengthening [9, 10]. The alloy has poor processability because of its high alloying degree. In the view of the lack of the reports about the researches and manufacture process of the GH3535 alloy seamless pipe at home and abroad, JIULI starts the GH3535 alloy seamless pipe research and development supported by Chinese Academy of Sciences Shanghai Institute of Applied Physics. JIULI successfully develops the sizes from Φ13.72 to Φ168 mm as per different specifications of seamless pipe, adopting the proper forming process of hot extrusion, cold processing technology and heat treatment process.

## Materials and Experimental Procedure

**Materials**. The GH3535 alloy was smelted by vacuum induction melting and vacuum consumable arc remelting (VIM+VAR) method. The designed chemical composition (wt%) of GH3535 alloy is listed in Table 1. After the homogenization treatment, the smelted GH3535 alloy was hammer cogged to a round bar. The hot extrusion process of the GH3535 alloy was performed on a 42MN steel extruder with a glass lubricant. The temperature of hot extrusion process was between 1150 and 1250 °C. Then the cold rolling process of the GH3535 alloy seamless pipe was performed in the cold rolling mills such as LG180, LG60, LG15.

**Experimental procedure**. The microstructures of the GH3535 alloy were observed by Zeiss metallographic microscope and Hitachi-3400 N scanning electron microscope (SEM). The flattening test and the flaring test of the GH3535 alloy seamless pipe were performed according to GB/T 246 and ASTM B829 standards, respectively. The sample for flattening test was about 65 mm in length, and the flattening coefficient was 0.09. As for the flaring test, the dilution rate was 30% of the outer diameter and the flaring top cone angle was 60°. The tensile test of the GH3535 alloy seamless pipe was performed using a Zwick test machine.

The corrosion rate of the GH3535 alloy seamless pipe was measured by static molten salt corrosion test at 700 °C for 400 h. The weight loss per unit area of the sample and the diffusion depth of Cr were calculated. The relevant metal ion concentrations in the molten salt environment before and after corrosion were detected.

**Table 1** Chemical composition of GH3535 alloy (wt%)

| C | Cr | Mo | Fe | Si | Mn | Al + Ti | Co | Ni |
|---|---|---|---|---|---|---|---|---|
| 0.04 | 8 | 18 | 3.5 | 0.5 | 0.8 | 0.3 | 0.02 | Bal. |

## Results and Analysis

**Microstructure Characteristics of GH3535 Alloy Round Steel**. Figure 1 shows the organizations of the raw material. A great amount of precipitates could be observed in the matrix, which is distributed in stripes, as shown in Fig. 1a. Based on the energy dispersive spectrometer (EDS) analysis, as shown in Fig. 1b, c, it could be concluded that the precipitates are rich in Mo and Ni. This type of carbide is commonly named as $M_6C$ phase, which is mainly formed in the liquid phase solidification process. The $M_6C$ phase particles are mainly distributed in the grain boundaries or the dendritic grain boundaries [9–11].

Previous studies showed [12, 13] that the $M_6C$ phase has a high recovery temperature. After the heat treatment at a high temperature (from 1220 °C to 1260 °C), the amount of $M_6C$ carbides is significantly decreased. The precipitation of carbides would reduce the high temperature plasticity of the alloy and increase the deformation resistance.

**Microstructure Characteristics and performance of GH3535 Alloy hot extrusion pipe**. Figure 2 shows the phase precipitation characteristics curve of GH3535 alloy. The hot extrusion temperature is between 1150 °C and 1250 °C obtained from the characteristic curve.

Figure 3a shows the outside surface of hot extrusion pipe after pickling, no pits, scratches and other defects can be observed. Figure 3b shows the inner surface of hot extrusion pipe which has no cracks, folds and other defects. It follows that the hot extrusion temperature is reasonable between 1150 °C and 1250 °C. If the

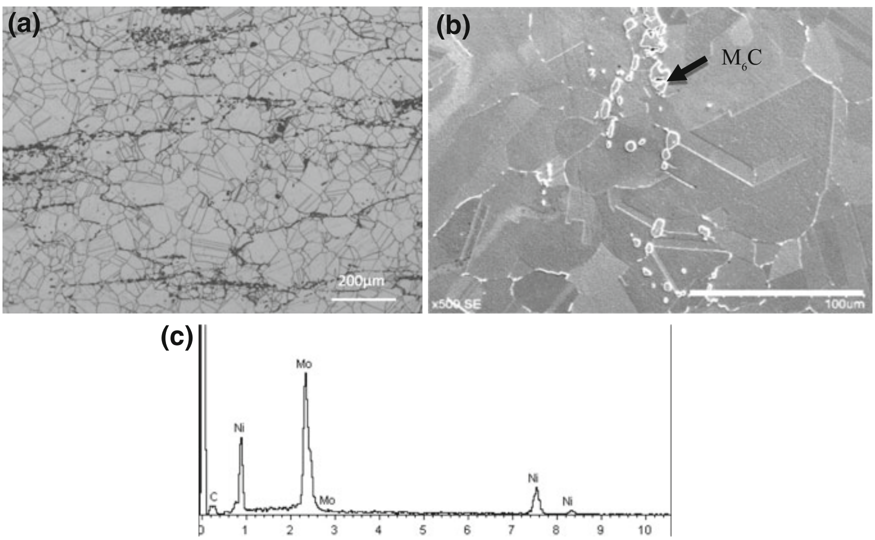



**Fig. 1** Raw material organization: **a** Microstructure, **b** scanning electron microscope, **c** EDS analysis

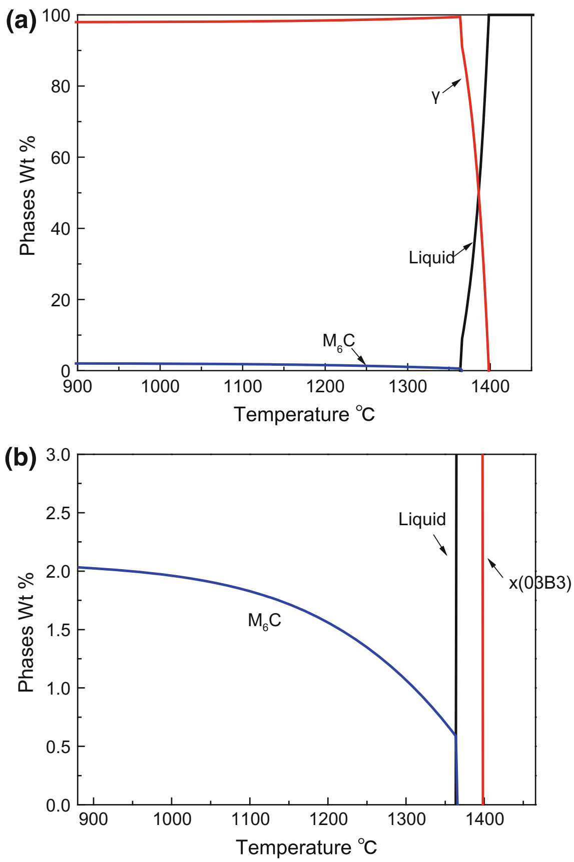



**Fig. 2** Phase precipitation characteristics curve of GH3535 alloy: **a** phase diagram of GH3535 alloy, **b** local phase-portrait

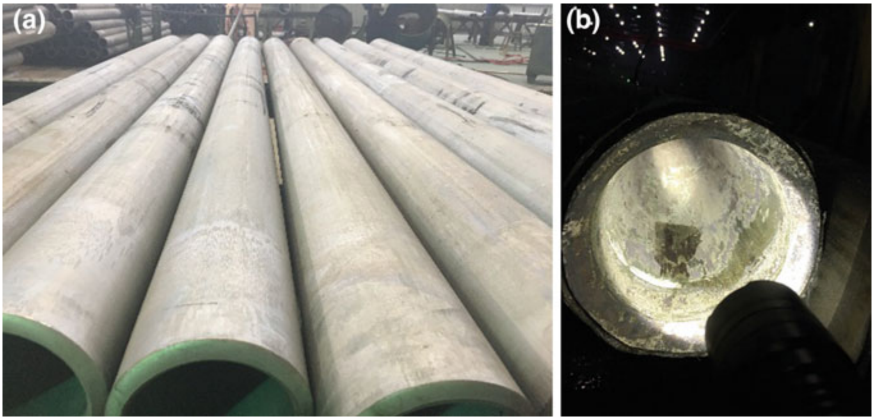



**Fig. 3** Extrusion pipe morphology: **a** outside surface, **b** inner surface

temperature is lower than the specified value, the hot extrusion will be fail, otherwise, the hot extrusion pipe is stratified when the temperature is higher.

The good plasticity and excellent performance of finished pipes could be achieved by cold deformation after annealing treatment, based on the extruded pipe with a good tissue uniformity. Figure 4 shows the grain size map of the extrusion tube head, middle and stern. It seems that a full dynamic recrystallization has been occurred in the processing of extrusion, which has formed equiaxed grains and uniform organization. The average grain size of the tube head is about 37.5 μm, the middle is about 38 μm, and the end is about 67 μm.

Figure 5a shows the SEM image of extrusion pipe. It seems that large pieces of precipitation are in the longitudinal direction and a little precipitation in grain boundary. The precipitates are still rich in Mo, Ni phase as shown in Fig. 5b.

Annealing treatment of the extrusion pipe should be performed before the cold deformation for a good deformation performance. Figure 6 shows the comparison of extrusion pipe mechanical properties before and after annealing treatment. It seems that the tensile strength is lower, the yield strength decreases significantly and the elongation of Normal temperature to 600 °C changes a litter, but the elongation is significantly increased at 650–700 °C high temperature.

**Microstructure of GH3535 alloy Seamless pipe**. The GH3535 alloy seamless pipe has a uniform microstructure in the length direction as shown in Fig. 7. The average grain size is 37–70 μm among the head, middle and stern of the GH3535

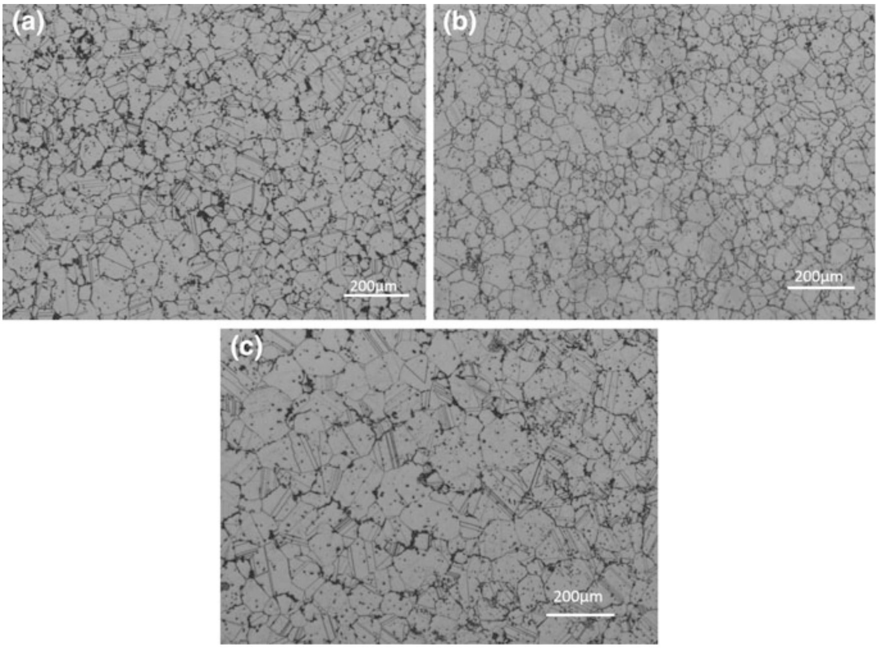



**Fig. 4** Grain sizes of extrusion pipe indicate the area of head (**a**), middle (**b**), stern (**c**)

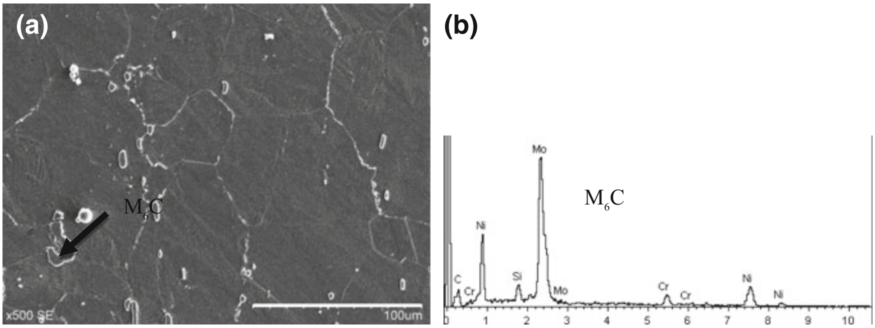
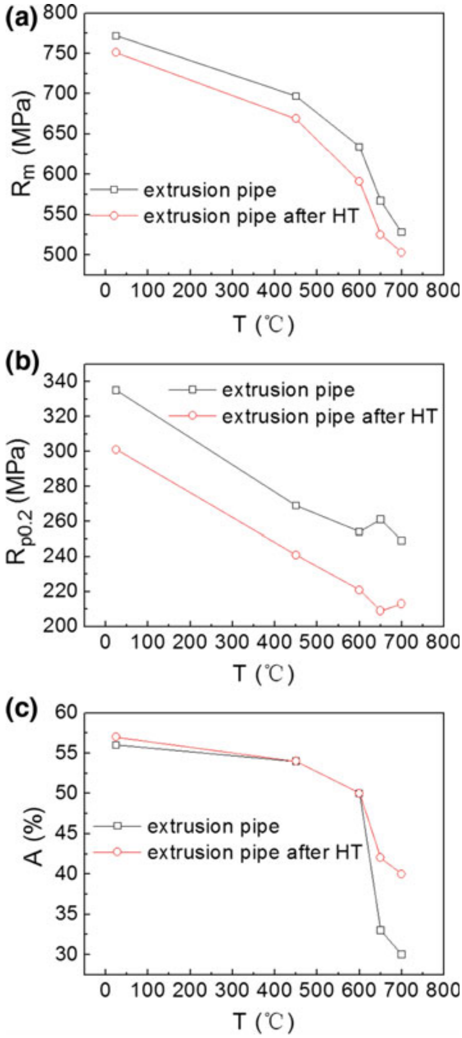



**Fig. 5** SEM of extruded pipe (**a**) and EDS analysis (**b**)

**Fig. 6** Comparison of mechanical properties of the extrusion pipe before and after annealing treatment: **a** the tensile strength, **b** the yield strength, **c** the elongation



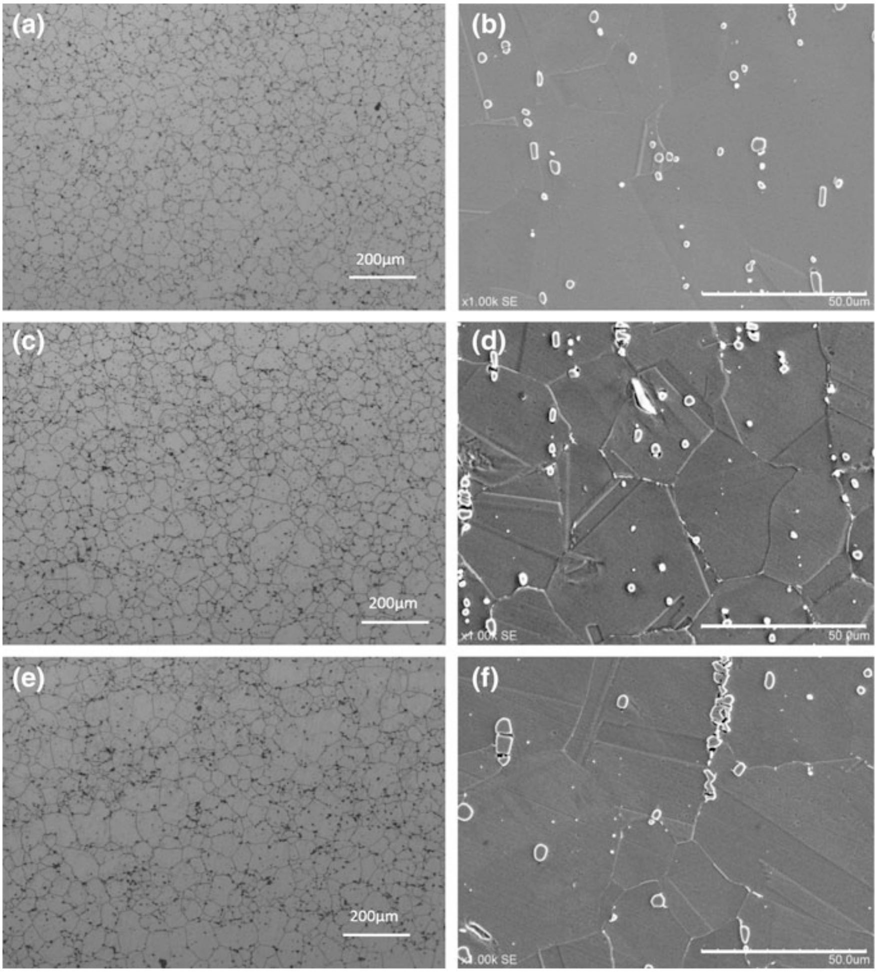



**Fig. 7** Grain size of pipe head (**a**), middle (**c**), stern (**e**), the SEM of pipe head (**b**), middle (**d**), stern (**f**)

alloy pipe. On the other hand, the GH3535 alloy seamless pipe still has large pieces of precipitation in the longitudinal direction as the same as the matrix, as shown in Fig. 8. Although the primary carbides is hardly to dissolve, it plays a strengthening role with dispersed in transgranular. The grain boundary on the basic precipitation has no precipitation with strictly heat treatment.

**Mechanical properties of GH3535 alloy Seamless pipe**. Figure 8 shows the mechanical properties of different seamless pipes (Φ168, Φ76, Φ13.72 mm) at room temperature and high temperature (450 °C, 600 °C, 700 °C). It seems that as the test temperature increased, the tensile strength and yield strength are decreased a downward trend, and the elongation is also decreased. The tensile strength and yield

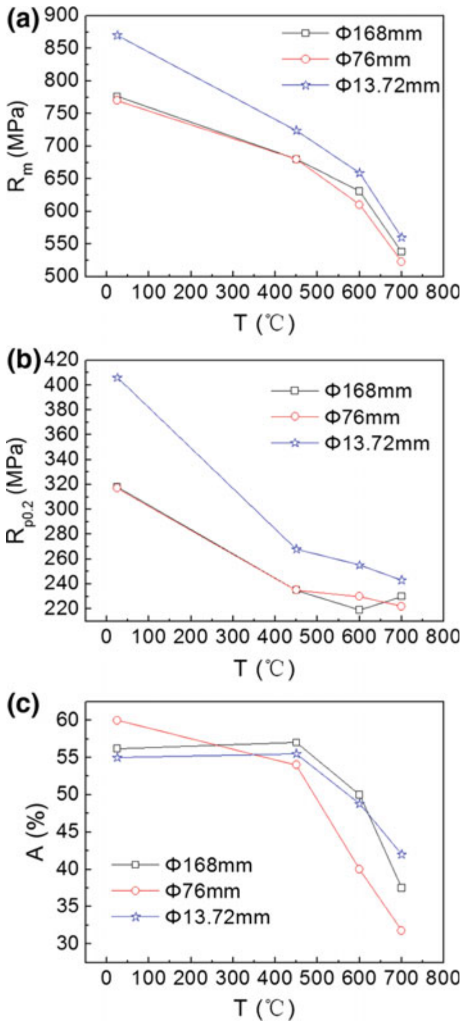



**Fig. 8** Comparison of mechanical properties of the pipes: **a** the tensile strength, **b** the yield strength, **c** the elongation

strength has no difference, and the elongation is close among different seamless pipes. Furthermore, the pipes have a high yield strength at 600–700 °C temperature, and the elongation can reach more than 35%.

Besides, the GH3535 alloy seamless pipes have no cracks or openings after technological test such as flaring and flattening test. The seamless GH3535 alloy pipes have good processing performance such as tube plate welding, bending and other process requirements.

**Corrosion resistance in molten salt of GH3535 alloy**. Table 2 shows the content of Cr after the molten salt corrosion test and depth of diffusion for element Cr in the molten salt corrosion environment (FLiNaK) in a molten salt at 700 °C for

**Table 2** the content of Cr after the molten salt corrosion test

| No. | The content of Cr after the molten salt corrosion test/[ppm] | The diffusion depth of Cr element/[μm] |
|---|---|---|
| The original state | 59 | / |
| 1# | 148 | 7–8 |
| 2# | 151 | 9–10 |
| 3# | 143 | 8–9 |
| 4# | 148 | 8–9 |

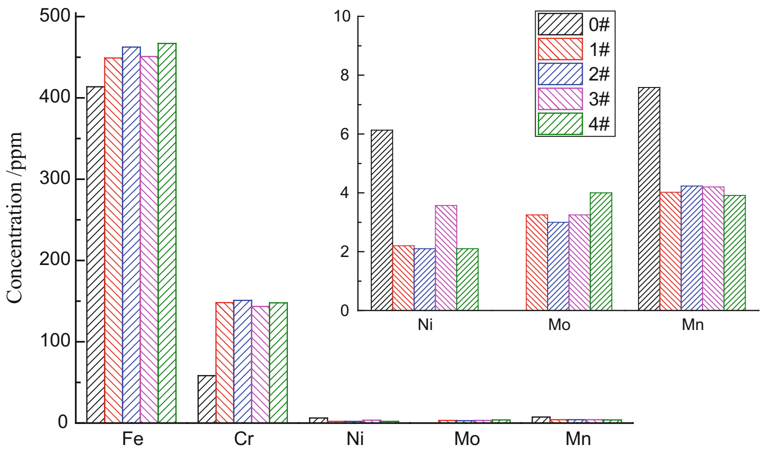



**Fig. 9** Content of various elements after the molten salt corrosion test: 1#(Φ114.3 mm), 2#(Φ88.9 mm), 3#(Φ76 mm), 4#(Φ13.72 mm)

400 h. It can be seen that the GH3535 alloy seamless pipes have good corrosion resistance in the molten salt corrosion environment.

Figure 9 shows the content of various elements after molten salt corrosion test at 700 °C for 400 h. It seems that the content of the elements in the molten salt is not much difference after the corrosion. It confirms that there is no significant difference in the corrosion resistance of the GH3535 pipes in the molten salt corrosion environment.

Figure 10 shows the weight loss per unit area of sample of four kinds of pipes (Φ114.3, Φ88.9, Φ76, Φ13.72 mm) after the molten salt corrosion test. It can seem that the corrosion rate of the pipe is low, the weight loss per unit area is less than 0.05 mg/cm$^2$, except individual pipe is negative growth.

According to the activity of the elemental composition, the more active Cr can replace the Fe in the ionic state, and the Fe deposition on the surface of the alloy caused by the displacement reaction may cause the weight gain of the sample, and on the other hand some impurities adhered to the sample surface may cause weight gain, too. The specific reasons need to combine the other test data for analysis and evaluation.

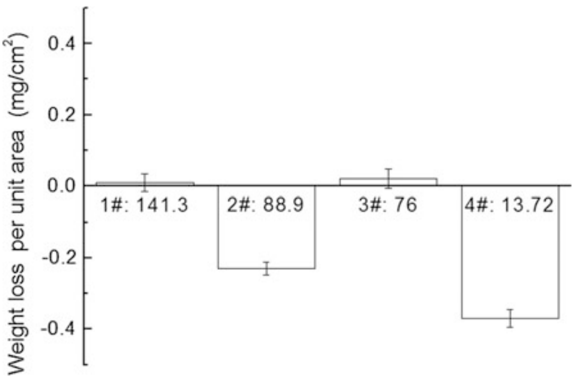



**Fig. 10** Weight loss per unit area of sample after the molten salt corrosion test

# Conclusion

The GH3535 seamless pipe was developed by the hot extrusion of the glass lubricant and multi-pass cold rolling between 1150 °C and 1250 °C.

The mechanical properties of GH3535 seamless pipe can be enhanced at room temperature, which the tensile strength can reach 800 MPa, the yield strength can reach 300 MPa, and the elongation is about 55%. Meanwhile, the yield strength of GH3535 seamless pipe is above 200 MPa and the elongation is more than 35% at 600–700 °C temperature.

The corrosion rate of the GH3535 alloy seamless pipe may be reduced, which the weight loss per unit area is less than 0.05 mg/cm$^2$, except individual pipe is negative growth. So the further research needs to be done.

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