Influence of Silicon, Boron and Rare-Earth Metals on Corrosion Resistance of Austenitic Chromium-Nickel Steel

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Abstract—The effect of silicon (in range 0.14–0.78 wt %), boron, and rare-earth metals (REM) on the corrosion resistance of low-carbon austenitic chromium-nickel steel of 03Kh18N11 (AISI 304L) grade was studied. It is shown that all steels in the quenched state when tested in boiling 56 and 65% HNO\textsubscript{3} solutions have comparable corrosion rates, which do not exceed the critical norm (0.5 mm/year) in accordance with GOST 6032–2017 (State Standard). Testing samples in boiling 27% HNO\textsubscript{3} + 4 g/L Cr\textsuperscript{6+} solution are susceptible to intergranular corrosion (IGC). The corrosion rate and the penetration depth of IGC increase with additional silicon concentration from 0.14 to 0.78 wt %. The study focused on the effect of nitric acid concentration and test temperature has shown that steel with 0.78 wt % Si has significant corrosion losses exceeding the critical ones when testing in 56 and 65% HNO\textsubscript{3} solutions with temperature of 120 and 130°C. But steel with high silicon content (0.78 wt %) and low carbon concentration (0.020–0.022%) after quenching in a range of 1080–1150°C and tempering at 650°C does not exceed the critical norm on average corrosion rate. Only 0.01 wt % increase in carbon concentration leads to a significant (more than 30 times) increase in corrosion rate of sensitized steel. It is shown that microalloying with REM does not impair corrosion resistance of sensitized steel. In contrast to REM, alloying chromium-nickel steel with even a small addition of boron (0.0015%) reduces steel corrosion resistance by an order of magnitude. Corrosion rate inverse dependence on quenching temperature is observed when, with increasing temperature, corrosion rate of 02Kh18N11 GS0.38R steel increases.

Keywords: silicon, boron, cerium, rare-earth metals, austenitic steel, corrosion resistance, intergranular corrosion, hexavalent chromium

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INTRODUCTION

At present, the mechanism problem of the segregation effect of impurity elements (such as silicon) included in a large number of austenitic steels at the amount of 0.2 to 1.0 wt %, boron, and rare-earth metals (REMs) on the intergranular corrosion (IGC) of stainless steels in strongly oxidizing media is controversial [1–10].

Silicon along with chromium is a ferrite-forming element and its effect is stronger by the factors of two—three. Addition of silicon to chromium—nickel stainless steels as alloying element increases scale resistance, decreases susceptibility to carburization, narrows γ-region, accelerates precipitation of σ-phase, improves casting characteristics and under particular conditions the composition of aggressive environment, and improves corrosion resistance [9–15]. On the contrary, an increase in the silicon content has an adverse effect on hot pressure treatment due to the decrease in the ductility of steels [16–19]. At the same time, low additives of REMs and boron increase the plasticity of austenitic steels in hot state [20, 21].

The aim of this work is to evaluate the effect of the silicon concentration (in the range of melted grade compositions of 0.14–0.78 wt %), boron, and REM on the propensity for IGC in strongly oxidizing medium.

MATERIALS AND METHODS

A total of three casts based on 02Kh18N11 steel with the silicon concentration of 0.14, 0.38, and 0.78% (here and further, by weight) were performed (1, 2, and 5, respectively, in Table 1).

The effect of boron and REM on the corrosion resistance of steel was studied after fractional casting of the melt with the silicon content of 0.38%, during which 0.0015% of boron was added to one ingot and
0.042% of REM was added to another ingot (3 and 4, respectively, in Table 1).

The casted ingots were exposed to peeling and, then, deformed using open forging and rolling to the blanks with required cross-section according to the conditions employed for the strain of stainless austenitic steels along with cooling of metal in the air.

The blanks of the stainless steels were exposed to quenching into water on austenite from 1050 to 1150°C. Heating was performed in electrical furnaces. The time of heating was 30 min in all cases. Sensitization heating was performed at the temperature of 650°C for 1 h.

The microstructure of the steels was studied using Carl Zeiss Axio Observed and Neophot-32 optical microscopes equipped with a digital video camera and the image input system.

The specimens were prepared for corrosion tests according to GOST 6032–2017 (DU method). Corrosion resistance tests of the steels with variable silicon content were carried out in nitric acid with the concentration of 20, 40, 56, and 65% and in the solution containing 27% HNO₃ and 4 g/L Cr⁺⁶ at the temperatures of 100, 120, and 130°C. Nitric acid with initial concentration of 65% according to GOST 11125–84 was used for experiments. Other solutions were prepared by diluting 65% HNO₃ with distilled water up to the required concentration. Cr⁺⁶ ions were added to the solution in the form of potassium bichromate K₂Cr₂O₇ additive.

The flasks equipped with a reflux condenser and closed heating mantles were used for tests of the specimens that are (6–10) × 20 × 80 mm in size in boiling solutions.

Special flasks (test tubes), which were sealed and transferred to a drying furnace equipped with a contact thermometer, were used for tests at other temperatures. The sizes of test specimens in test tubes corresponded to 5 × 10 × 20 mm. The corrosion rate was determined according to the weight loss of two independent specimens tested in parallel. In this case, one of the specimens was prepared in the form of metallographic polished section for further microscopy observation of the character of steel etching. After corrosion resistance tests, a cross section was made on one out of two specimens, which was further polished in order to measure the penetration depth of IGC.

The maximum allowable (critical) degree of corrosion losses was considered the rate of corrosion of 0.5 mm/year according to the requirements of GOST 6032–2017.

**RESULTS AND DISCUSSION**

Table 2 shows the results of five test cycles of the specimens quenched in water from 1080°C after exposure in boiling 56 and 65% HNO₃ for 30 min.

The specimens in austenite-quenched state possess comparable rates of corrosion of less than 0.28 mm/year. The dependence of total weight loss on the silicon content was not revealed in these tests. All tests were carried out at constant microscopy observations of polished sections; this allowed us to reveal the difference in the behavior of grain boundaries of the steels depending on the silicon content (Fig. 1).

During the test of 02Kh18N11GS0.78 steel in boiling 56% HNO₃, grain boundaries were observed on polished section after a 2-h exposure, whereas the polished section of 02Kh18N11GS0.04 steel revealed these boundaries after exposure for 6 h. In this case, the etching form of grain boundaries of these steels is also different. Etching of the steel with a reduced (less than 0.20%) silicon content occurs along grain boundaries and (mainly) along boundaries of twins (Fig. 1a). In this case, etching of grain boundaries occurs non-homogeneously and is weaker. With an increase in the silicon content to 0.38%, the etching rate of grain boundaries increases and becomes comparable with the etching rate of twin boundaries (Fig. 1b). At the silicon content of 0.78%, grain boundaries are etched more intensely than twin boundaries (Fig. 1c).

Derived from the results on the behavior of grain boundaries depending on the silicon concentration in the austenite-quenched stainless steel, it can be suggested that an increase in the duration of tests under these conditions would result in the integral grain precipitating from the surface of the specimens possessing high silicon content (where etching of grain boundaries is more intense) at a particular time moment, when the penetration depth of IGC would exceed the grain

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**Table 1. Chemical composition of the studied steels**

| No. | Grade             | C     | Si    | Mn    | S     | P     | Cr    | Ni    | N     | microalloying |
|-----|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|---------------|
| 1   | 02Kh18N11GS0.14   | 0.022 | 0.14  | 1.01  | 0.011 | 0.012 | 17.82 | 11.21 | 0.05  | –             |
| 2   | 02Kh18N11GS0.38   | 0.021 | 0.38  | 1.00  | 0.012 | 0.012 | 17.80 | 11.20 | 0.04  | –             |
| 3   | 02Kh18N11GS0.38R  | 0.0015% B | 0.0420% REM |
| 4   | 02Kh18N11GS0.38Ch | 0.020 | 0.78  | 1.05  | 0.011 | 0.012 | 17.85 | 11.22 | 0.05  | –             |
size. In this case, this process would be much longer for the steel possessing low concentration of silicon, because corrosion propagation inside metal along twin boundaries occurs at a lower rate. This is caused by the fact that the probability to encounter a twin with the same plane under the first twin is extremely low after etching of the twin plane possessing low corrosion resistance. At the same time, IGC along grain boundaries penetrates at a very high rate, because it interacts with and destructs a new grain boundary, which is susceptible to corrosion, upon penetration of corrosion medium inside the metal.

Consequently, the weight loss of metal from the moment of individual grain precipitation from the steel possessing high silicon content and the difference of the corrosion rates with the steel possessing low concentration of silicon should drastically increase. Analysis of weight loss and metallographic study of polished sections after each cycle revealed that 02Kh18N11GS0.38R steel is more susceptible to IGC after microalloying with boron. After the first cycle of tests, grain boundaries could be clearly observed on the polished section (in analogy to high-silicon steel) (Fig. 1d), whereas grain boundaries were etched to a lower

### Table 2. Corrosion resistance test results of stainless steels in boiling nitric acid solution

| Concentration of element, wt % | Rate of corrosion by cycles, mm/year (1 cycle = 48 h) | Average rate of corrosion, mm/year |
|--------------------------------|------------------------------------------------------|----------------------------------|
|                               | I          | II         | III        | IV         | V          | 56% HNO₃       |
| 0.022 0.14                    | 0.264      | 0.177      | 0.143      | 0.132      | 0.179      | 0.179          |
| 0.021 0.38                    | 0.256      | 0.135      | 0.129      | 0.137      | 0.164      | 0.164          |
| 0.020 0.78                    | 0.250      | 0.100      | 0.118      | 0.148      | 0.157      | 0.155          |
| 0.022 0.14                    | 0.296      | 0.192      | 0.199      | 0.177      | 0.126      | 0.198          |
| 0.021 0.38                    | 0.256      | 0.262      | 0.250      | 0.238      | 0.216      | 0.244          |
| 0.020 0.78                    | 0.270      | 0.255      | 0.231      | 0.244      | 0.202      | 0.240          |
| 56% HNO₃                      | 0.329      | 0.279      | 0.248      | 0.262      | 0.253      | 0.274          |
| 0.0015 B                      | 0.270      | 0.255      | 0.231      | 0.244      | 0.202      | 0.240          |
| 0.0420 REM                    | 0.358      | 0.171      | 0.166      | 0.156      | 0.154      | 0.200          |
| 65% HNO₃                      | 0.270      | 0.255      | 0.231      | 0.244      | 0.202      | 0.240          |

**Fig. 1.** Microstructure of stainless steels with different silicon content after 35 hours of testing in boiling 56% HNO₃: (a) 02Kh18N11GS0.14, (b) 02Kh18N11GS0.38, (c) 02Kh18N11GS0.78, (d) 02Kh18N11GS0.38R, and (e) 02Kh18N11GS0.38Ch.
extent in the specimens of initial 02Kh18N11GS0.38 steel (without boron). 02Kh18N11GS0.38Ch steel with REM additive showed higher propensity for IGC. After the first cycle of tests, grain boundaries were etched weakly and nonuniformly. In addition, etching also proceeded along twin boundaries (Fig. 1e). This etching character of polished sections was preserved until the end of tests.

Derived from metallographic studies, it can be stated that the addition of boron even at small quantities has an adverse effect on the propensity of stainless steel for IGC, whereas introduction of REM to steel would improve the resistance of grain boundaries.

In order to determine the limiting temperature and concentration of nitric acid, at which 02Kh18N11GS0.14 and 02Kh18N11GS0.78 steels with low and high concentration of silicon remain IGC resistant, the tests were carried out in nitric acid with the concentration of 20, 40, 56, and 65% at the temperatures of 100, 120, and 130°C. The tests showed that an increase in the concentration of acid and its temperature lead to the increase in corrosion losses of the steels (Fig. 2). In this case, a remarkable precipitation of grains from the surface of high-silicon 02Kh18N11GS0.78 occurs at the test temperatures of 120 and 130°C and the concentrations of acid of 56 and 65%, which drastically increases the rate of corrosion and corrosion losses. Grain precipitation in the steel possessing lower concentration of silicon was not observed. At lower temperatures and concentrations of nitric acid, corrosion losses of the steels are comparable.

For the more convincing determination of silicon effect under oxidizing conditions on the resistance of the boundaries of austenite-quenched steel, the tests were made stricter through the addition of Cr+6 ions to solution; for this purpose, the solution containing 27% HNO3 and 4 g/L Cr+6 was used.

Under strict test conditions (Table 3), all specimens demonstrated high susceptibility to IGC (more than 0.5 mm/year is observed); however, a clear dependence of corrosion damage of metal vs. silicon content dependence could be recorded. Precipitation of grains from the surface of the specimens on high-silica 02Kh18N11GS0.78 steel was already recorded at the first cycle of tests, which results in a significant weight loss of the specimen, while this effect was observed only at the second cycle of tests on other specimens. The steel possessing high concentration of silicon also possesses highest rates of corrosion by cycles and medium rate of corrosion and penetration depth of IGC.

Investigation of the corrosion resistance after sensitization heating are of large practical interest, because steels of this class are often exposed to welding or operate at high temperatures, that is, the tests according to DU method in GOST 6032–017. Table 4 and Fig. 3 show the results of corrosion tests of austenite-quenched stainless steels from various temperatures exposed to additional annealing for 1 h at 650°C, which results in carbide precipitation. It can be seen that the average rate of corrosion of the steel sensitized after quenching from 1080°C increases from 0.190 to 0.0489 mm/year, that is, by the factor of 2.0–2.5 with an increase in the concentration of carbon from 0.14% to 0.78% (at low (0.020–0.022%) concentration of carbon) (Table 4, option A); however, it does not exceed critical value of 0.5 mm/year according to GOST 6032–2017. An increase in the concentration of carbon by 0.01% results in a remarkable (from 0.489 to 1.6340 mm/year) increase in the rate of corrosion of sensitized steel containing 0.78% Si by more than the factor of 30.

An increase in the temperature of heating for quenching from 1080 to 1150°C (Table 4, option C) affects marginally corrosion resistance of the sensitized steel with the low concentration of carbon at the silicon concentrations under study (0.14, 0.38, and

![Fig. 2. Corrosion rate dependence of austenitic stainless steels with different silicon content ((1) 02Kh18N11GS0.14, (2) 02Kh18N11GS0.78) on nitric acid concentration and test temperature: (a) 100, (b) 120, and (c) 130°C.](image-url)
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0.78%) (Fig. 3, curve 3, 4, 6) and significantly decreases corrosion losses of 03Kh18N11GS0.78 steel possessing the carbon concentration increased by 0.010% (Fig. 3, curve 1). In this case, even after quenching from 1150°C, the corrosion rate of steel with an increased (0.030%) concentration of carbon remains quite high (1.443 mm/year).

Thus, at the increased (0.78%) content of silicon, but low (0.020%) concentration of carbon, the average corrosion rate of sensitized steel quenched from 1080–1150°C is less than the critical value of such steels, whereas an increase in the concentration of carbon by 0.01% results in a significant (by the factor of more than 30) increase in the corrosion rate of sensitized steel.

It was mentioned in [22, 23] that an increase in the concentration of silicon in similar austenitic steels AISI 304L (03Kh18N11) containing 0.03% C also increases their susceptibility to IGC in oxidizing medium after exposure at the temperatures below 650°C. At the same time, alloying of Kh20N20 steel containing less than 0.032% carbon with more than

### Table 3. Corrosion resistance test results of quenched stainless steels in boiling solution of 27% HNO₃ + 4 g/L Cr⁺⁶

| Concentration of element, wt % | Rate of corrosion by cycles, mm/year (1 cycle = 24 h) | Average rate of corrosion, mm/year | Penetration depth of IGC, mm |
|-------------------------------|--------------------------------------------------|---------------------------------|----------------------------|
| C                | Si                  | I       | II       | III      | IV       | V       |                                      |
| 0.022  | 0.14               | 1.651   | 1.472   | 1.080   | 1.402   | 1.337   | 1.370   | 0.025                           |
| 0.021  | 0.38               | 1.962   | 2.354   | 3.401   | 4.033   | 4.883   | 3.325   | 0.137                           |
| 0.020  | 0.78               | 2.550   | 3.117   | 7.456   | 7.783   | 8.393   | 5.864   | 0.192                           |

The values that characterize unsatisfactory propensity for IGC are highlighted in bold.

### Table 4. Corrosion resistance test results of sensitized stainless steels in boiling 65% nitric acid solution (quenching at 1080°C (Option A), at 1120°C (Option B), at 1150°C (Option C), 30 min, in water and sensitizing heat treatment 650°C, 1 hour, on air)

| Concentration, wt % | Rate of corrosion by cycles, mm/year (1 cycle = 48 h) | Average rate of corrosion, mm/year |
|---------------------|--------------------------------------------------|-----------------------------------|
| C                  | Si                  | microalloying | I | II | III | IV | V |
| 0.022  | 0.14               |               | 0.164 | 0.179 | 0.227 | 0.190 | 0.190 | 0.190 |
| 0.021  | 0.38               |               | 0.249 | 0.243 | 0.243 | 0.252 | 0.255 | 0.248 |
| 0.0015 B |               |               | 0.308 | 1.193 | 2.981 | 2.673 | 5.379 | 2.506 |
| 0.0420 REM |               |               | 0.229 | 0.229 | 0.226 | 0.210 | 0.277 | 0.234 |
| 0.020  | 0.78               |               | 0.285 | 0.397 | 0.563 | 0.524 | 0.676 | 0.489 |
| 0.030  |                   |               | 1.116 | 7.331 | 28.60 | 21.33 | 23.37 | 16.340 |
| 0.022  | 0.14               |               | 0.173 | 0.188 | 0.182 | 0.193 | 0.245 | 0.196 |
| 0.021  | 0.38               |               | 0.352 | 0.313 | 0.291 | 0.275 | 0.236 | 0.293 |
| 0.0015 B |               |               | 0.283 | 1.337 | 3.019 | 3.190 | 5.434 | 2.652 |
| 0.0420 REM |               |               | 0.229 | 0.205 | 0.203 | 0.235 | 0.274 | 0.229 |
| 0.020  | 0.78               |               | 0.330 | 0.338 | 0.599 | 0.582 | 0.654 | 0.501 |
| 0.030  |                   |               | 0.363 | 0.748 | 1.120 | 4.310 | 16.72 | 4.650 |

The values that characterize unsatisfactory propensity for IGC are highlighted in bold.
3.29% silicon inhibits IGC in this steel regardless of the time of exposure from 1 to 100 h [24]. However, an increase in the silicon content to 5.4% in the same steel containing 0.0015% C and 0.1% P drastically decreases its passivating ability [25].

It was also determined in this work that microalloying with rare-earth elements do not impair the corrosion resistance of the sensitized steel (Table 4, curves 4, 5). In contrast to REM, alloying even with low (0.0015%) boron decreases the corrosion resistance by one order. In the case of boron-microalloyed steel, there is an inverse dependence of the corrosion rate on the temperature of quenching (Fig. 3, curve 2): the corrosion rate of 02Kh18N11GS0.38R steel increases from 2.506 mm/year after quenching from 1080°C to 5.596 mm/year after quenching from 1150°C with an increase in the temperature of heating for quenching.

The latter fact is presumably caused by the increase in the grain size and, accordingly, enrichment enhancement of grain boundaries and near-boundary zones with boron, which is known to be a horophilic element and practically insoluble in iron.

**CONCLUSIONS**

It has been determined that there is no dependence of total weight loss on the silicon content in chromium—nickel austenitic steel with the variable (within the grade composition) concentration of silicon (0.14–0.78%) in the austenite-quenched state in 56 and 65% boiling aqueous solutions of nitric acid. The corrosion resistance of sensitized stainless steel is governed by individual and combined effects of carbon, silicon, boron, and REMs on the precipitation degree of chromium carbides along grain boundaries. Limitation of the carbon concentration to less than 0.020% and silicon to less than 0.20% could result in a manifold increase in the corrosion resistance of stainless chromium—nickel steel of Kh18N11 type.

An increase in the temperature of heating for austenite quenching is one of the approaches to fight against IGC, which reduces corrosion losses of steel. The more complete dissolution of the carbide phase and more uniform distribution of impurity atoms along grain solid could be achieved with an increase in the temperature of heating for quenching, thus decreasing its segregations near grain boundaries.

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