The corrosion resistance investigation of the austenitic nitrogen Cr-Mn-Ni-Mo-N steel in the cast and deform state

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Abstract. In the article are given the analyzing corrosion resistance data of nitrogen containing steels. The resistance on the pitting, crevice corrosion with high nitrogen containing is estimated. The corrosion resistance of the steel 05Kh22AG15N8M2F in the condition after cold deforming in chloride containing substances is defined. Laboratory and field tests two types of steels 05Kh22AG15N8M2F and 12Kh18N10T are provided. It’s determined that the samples of the steel 05Kh22AG15N8M2F are demonstrating larger corrosion resistance at the laboratory and field investigations in comparison with the steel 12Kh18N10T. The properties of the steel 05Kh22AG15N8M2F with known AISI 316 are compared. It is established that the steel 05Kh22AG15N8M2F a top of AISI 316 on the resistance to the pitting corrosion and the critical pitting temperature. Pitting Resistance Equivalent (PREN) for the steel 05Kh22AG15N8M2F and the critical pitting temperature are determined.

1. Introduction

The intergranular (ICC), pitting and crevice corrosion present a problems for the stainless steels and one of the ways to solve this unacceptable phenomenon – the alloying by nitrogen. As known, nitrogen improve the resistance of the austenitic steels to the corrosion, especially for the local corrosion form.

In the highlowcarbonnitrogen steels ICC can develop from the formation not carbides, but a nitrides chromium, such as Me2N. In this case, ICC slow down because of the less depletion border areas by chromium. Conditions beginning ICC in the result formation nitride Me2N in the steel X24H20 were studied [1]. To explanation the influence of nitrogen on ICC resistance steel O3X19AG3H10 studied to ICC after the temper in comparison with changes of condition of the grain boundary zone [2]. It’s shown that ICC regardless of the test method, was determined by release of carbides during the tempering, not nitrides. At the same time, the tendency to ICC decreased with the increasing nitrogen content, but the width of the chromium-depleted border zone did not depend on nitrogen content (the latter investigated using transmission electron microscopy). From the data obtained by the authors, it concluded that nitrogen does not affect diffusion processes, but changes in the energy state of the boundaries. Experiments have shown that with an increase in nitrogen content, the relative free energy of the boundaries is decreasing. The formation of the particles of a new phase should be accompanied by a decrease in free energy ΔF. During the formation of the particles at the grain boundaries:

\[ \Delta F = -V \cdot \Delta fV + S \sigma + Z - \Delta F_b, \]  

(1)
where \( V \) – volume; \( \Delta fV \) – variation of free energy per unit of volume of the formed particle; \( S \) – summary quantity of the particle surface; \( \sigma \) – unit surface energy on border particle-matrix; \( Z \) – elastic energy arising due to the differences in a specific volumes of a particle and matrix; \( \Delta F_b \) – difference of border energy. Because of nitrogen injection reduces \( \Delta F_b \), then \( \Delta F \) increases. Since a probability carbide nucleus formation, than with increasing \( \Delta F \) probability carbide formation decreases. The obtained ideas about the effect of nitrogen on the energy state of a grain boundaries, apparently, can also be used in explaining the effect of nitrogen on the other properties of the corrosion-resistant steels [3].

A summary of the above and previously known data indicates the positive effect of nitrogen on the increasing in the resistance against ICC. However, it should be keep in mind, that the stability chromium nitride \( \text{Cr}_3\text{N} \) lower the stability carbide \( \text{Cr}_3\text{C}_6 \) in the hardened chromium-nickel and chromium-nickel-manganese austenitic steels in the wide range of the potentials, as a result chromium nitrides can be etched [4]. Carbo-nitride, such as \( \text{Cr}_2(\text{C}_x\text{N}_y) \) have significantly more higher resistance, than \( \text{Cr}_2\text{N} \). Therefore, to ensure the maximum corrosion resistance of nitrogen-containing steels, it is advisable to choose the heat treatment that ensures the absence or minimum amount of the nitride precipitates [3].

The pitting corrosion is one of the well-known problems for the stainless steels. It can also be sensitized, especially any local Cr decreasing can provide the pitting corrosion. Thus, any chromium segregation caused by the welding or the heat treatment, etc., may have an effect on the pitting formation resistance.

The critical pitting temperature determines the temperature of the whole formation. The general range of this temperature for the corrosion resistant steels is 10–100 °C and depends from the composition of the chemical composition of the steel. A source [5] reports, that the crevice corrosion critical temperature lies on 20°C below the pitting formation critical temperature (Figure 1) [6]. The conventional pitting resistance index for the corrosion resistance steels with nitrogen – Pitting resistance equivalent + N (PREN), is determined as:

\[
\text{PREN} = \text{Cr} \text{ (\%)} + 3,3 \text{ Mo (\%)} + x \text{ N (\%)},
\]

where \( x = 13 \ldots 30 \).

The author [7] suppose, that \( x=16 \) using for the steels with a molybdenum containing to 4,5 % and \( x=30 \) for the steels with a molybdenum containing 4,5-7,0 %.

The authors [6] suggesting own version to the calculation pitting resistance critical temperature, instead of PREN index they suggesting MARC («Measure of Alloying for Resistance to Corrosion»):

\[
\text{MARC} = \%\text{Cr } + 3,3\%\text{ Mo } + 20\%\text{ N } + 20\%\text{C } - 0,5\%\text{Mn } - 0,25 \%\text{ Ni},
\]

On figure 1 performed the pitting formation critical temperatures some of commercial alloys. The authors approve that chromium, molybdenum, carbon and nitrogen (in the solid solution) increasing the corrosion resistance, while Mn and Ni slightly reduce it.
Crevice corrosion, in generally, follows the same principles (that shown by second dependence on figure 1), such as the pitting, but the conditions here significantly harder because of geometrical influence (electrolyte condensed in the crack) [8].

2. Corrosion resistance investigation of high nitrogen steels

The pitting, crevice and corrosion cracking in significantly interconnecting and typical for the substances, containing chloride-ions or other halide ions. The pitting and crevice corrosion resistance in the chromiumnickel-molybdenum steels increasing with nitrogen insertion to them [3]. So, the investigation of chromiumnickel-molybdenum austenitic steels with the different content of nitrogen (from 0,08 to 0,39 %) and manganese (0,9-4,8 %) let to determined, that even with a relatively high content of manganese and sulfur, the influence of 0,38% N provides high resistance to the pitting [9].

Increasing the pitting and crevice corrosion resistance in the high alloyed steels such as 20Cr-25Ni and 20C-25Ni-4,5Mo with the presence 0,21 % N [10]. The achieved effect is associated with the formation of an ammonium ion NH\textsubscript{4}+, which increases the pH of the solution and facilitates the repassivation. A positive effect of a nitrogen influence was find in the steel as with molybdenum, so without him, and this showing on a possibility of the creation the economically alloyed steels without molybdenum and resistant to the pitting and crevice corrosion. For example, the results of the investigation of the austenitic steels without molybdenum with 20 % Cr and 10 % Ni with a super equilibrium nitrogen containing – 0,7 % N showed the pitting potential ≥0,90 V (for comparison – pitting potentials the same steel, but with 0,35 % N and also for the steel type X17H13M2 and X18H10 respectively consist 0,35; 0,30 and 0,18 V) [11].

Analyzing the given information on the corrosion resistance of the nitrogen-containing steels, we can conclude that to provide higher, which for the steels of the type 18-10 corrosion resistance, the steel should contain more than 18% Cr in its composition, should be alloyed with a molybdenum and nitrogen. The content of austenite-formation elements Ni and Mn should ensure the austenitic structure of the steel (including due to the influence of Mn on the solubility of nitrogen, a strong element - austenitizing agent in iron-based solid solutions).

In this work the next compounds of the cast nitrogen steels were studied – table 1.
The results of inspection of the surface of the test samples for the subject of absence and intensity the corrosion substance, but also on tested. Really, inspecting tested ICC samples even in a cast, most a heterogeneous structural condition, downturn to the angle 90 °, showed the absence of a cracks not only on the sample, which was not exposed in a corrosion substance, but also on tested. The steel in condition after annealing at 1200 °C more don’t show the signs of ICC [14, 15].

With the tests on the pitting corrosion the cast samples after the heat treatment: (1) the annealing at 1200 °C, 1 h, the hardening in the water and (2) the annealing at 1200 °C, 1 h, the hardening in the water and the provocative aging at 700 °C, 100 h was compared. The results of inspection of the surface of the test samples for the subject of absence and intensity the pitting corrosion damage in the dependence of the continuance of exposure in the solution of iron trichloride and the temperature of the test are given, respectively, in the tables 2 and 3 and on the...
From the data presented in the table 2 it is obviously, that at 25 °C, with the increasing continuance of exposure from 1 to 10 h, there is no practical difference in the resistance against the pitting corrosion of the cast metal in the hardened state and the metal after the hardening and the additional provocative aging.

**Table 2.** The results of the visual inspection of the surface of the cast steel 05Kh22AG15N8M2F samples after the tests on the resistance to the pitting corrosion after the two types of the heat treatment: 1 – annealing at 1200 °C, 1 h, hardening in the water; 2 – annealing at 1200 °C, 1 h, hardening in the water + provocative aging at 700 °C, 100 h.

| Heat treatment                                                      | Continuance of exposure in the solution, h |
|--------------------------------------------------------------------|-------------------------------------------|
| The annealing at 1200 °C, 1 h, hardening in water                  | 1                                         |
|                                                                    | 2                                         |
|                                                                    | 5                                         |
|                                                                    | 10                                        |
| The hardening in the water + the provocative aging at 700 °C, 100 h | No focuses of the pitting corrosion was detected |
|                                                                    | No focuses of the pitting corrosion in the concrete |
|                                                                    | No focuses of the pitting corrosion in the concrete |
|                                                                    | The single uneven distributed focuses of the pitting corrosion |

**Table 3.** The resistance of the steel 05Kh22AG15N8M2F after the annealing at 1200 °C, 1 h, the hardening in the water and annealing at 1200 °C, 1 h, the hardening in the water + the provocative aging at 700 °C, 100 h against pitting corrosion at 35-50 °C

| t, τ, °C h | Heat treatment | The view of the surface of the sample | RSD*, %/ | The mark of the resistance |
|-----------|----------------|---------------------------------------|----------|---------------------------|
| 35 5      | 1200 °C, 1 h, water | The small focuses of the pitting corrosion | 0,3 / 8  | 1200 °C, 1 h, water + 700 °C, 100 h | The pitting, such as at the hardening structure |
| 45 5      | 1200 °C, 1 h, water | The many smallest focuses of pitting corrosion | 1,0 / 6  | 1200 °C, 1 h, water + 700 °C, 100 h | The many focuses of the pitting corrosion |
| 50 5      | 1200 °C, 1 h, water | The irregularly distributed focuses of pitting corrosion of different sizes | 16 / 3   | 1200 °C, 1 h, water + 700 °C, 100 h | The many focuses of the pitting corrosion |

RSD* - The rate of the surface damage about by the scale ASTM DIN 610

According to the scale of the standard ASTM DIN 610 the corrosion resistance to the pitting corrosion is estimating by 10-rate scale of the sizes of the surface damage square (in %). The mark ~8 point is given at the damage square 0,1 %. On the surface in this case single linear focuses of the pitting corrosion are initiated. Such scene observed at the 10 h test. The provocative aging don’t degrade the resistance of the steel to the pitting corrosion: the appearance of the hardening and the aging samples after tests is perfect uniform, the low damage rate evidence about the resistance of the cast steel to the pitting corrosion under the given test conditions.

With rising the temperature of the test solution to 35-50 °C the pitting corrosion intensity is increasing. It should be particularly noted that the difference in the corrosion behavior between the steel in the hardened and aged state was also not observed, the appearance of the samples was the same (table 3). The sizes of damage focuses at the temperature 35 °C is still the small at the test period to 5 h. With rising the exposure continuance period of the solution with the temperature 35 °C the intensity of the pitting corrosion increasing, and, according to scale ASTM DIN 610, she consist of 1 % (the rate of the resistance 6). At the test 5 h at 45 °C immunity to the pitting corrosion abruptly...
reduced (to rate 3), on the surface at the same time the smallest microfocuses the focuses of the pitting corrosion are initiating. Based on the figure 1, it’s can considering that for the 05Kh22AG15N8M2F cast steel, which have PREN = 33.2 in the hardened and also in the aging condition, the value of the critical pitting formation temperature is up to \( t_{\text{crit}, \text{P}} = 43 \) °C (Figure 2). With increasing the test temperature to 70-80 °C it’s take a place the intensive common solution of the samples surface, the pitting formation potential is going down because of prevailing the velocity of general corrosion over a pitting growth velocity. (It should be consider, that initiation of the focuses of the pitting corrosion determined not only by chemical composition, but also (in specific stage) by the presence of microdefects of the casting at the pitting resistance of the cast metal product estimation).

![Figure 2. The influence of the test temperature in the 10% FeCl\textsubscript{3} (5 h) on the damage pitting corrosion rate (RSD) of the samples of the steel 05Kh22AG15N8M2F](image)

The comparison of the properties of the steel 05Kh22AG15N8M2F with the well-known steel AISI 316 (table 4) showed, that the new cast nitrogen steel significantly exceed the steel AISI 316 in the pitting resistance corrosion – the coefficient PREN – 33 against 24 (at steel AISI 316) and the pitting formation critical temperature [14].

**Table 4. The comparison of the properties of the corrosion resistance of the steels 05Kh22AG15N8M2F and the steel AISI 316.**

| The mark                  | %Cr | %Mo | %N  | PREN\(^1\) | PCT\(^2\) (°C) |
|--------------------------|-----|-----|-----|------------|----------------|
| AISI 316                 | 16,5| 2,1 | 0,05| 24,2       | 15\(^2\)       |
| 05Kh22AG15N8M2F          | 22  | 1,5 | 0,5 | 33         | 43\(^3\)       |

\(^1\) Pitting resistance equivalent, PREN = %Cr+3,3%Mo+16%N;
\(^2\) Pitting formation critical temperature, PCT: by ASTM G-48A (at 72 h in the 6% FeCl\textsubscript{3} solution); \(^3\) by the Russia state standards (at 5 h in the 10% FeCl\textsubscript{3} solution).

3. Conclusions
Thus, it can be conclude, that: (1) the steel 05Kh22AG15N8M2F in the cast state, such as after the partially homogenizing the structure annealing at 1200 °C (1 h, the water), is not inclined to ICC due to the absence the influences of the excess phases particles on the grain boundaries and the other cast metal structural elements (2). The investigated steel in the state after the hardening (1200 °C, 1 h) and the hardening with further aging 100 h at 700 °C under the accelerated tests in 10 % solution FeCl\textsubscript{3} by the State Standard 9,812-89 at the temperature 25 °C and the exposition time in the substance up to 10 h, and also at the 35 °C, 5 h tests, is not demonstrating the pitting corrosion tendency. (3) For the studied steel, in the state after the hardening, the hardening and aging, pitting formation critical
temperature determined PCT = 45 °C - exceeding that for the traditional corrosion-resistant steels of the type 18Cr-8-12Ni.

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