COMPARATIVE STUDY ON THE CORROSION RESISTANCE OF SPECIMENS FROM NON-MODIFIED AND NANO-MODIFIED STEEL GX120Mn12

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The corrosion behavior of specimens of steel grade GX120Mn12 before and after nano-modification with a composition of $\text{TiCN} + \text{Y}_2\text{O}_3 + \text{Cr} + \text{Fe}$ in ratio 2:1:1:6 is studied. The method of cyclic immersion in different aggressive media such as solution of NaCl, MgCl_2 and MgSO_4 , and 3%NaCl is used. The indicators for mass loss and average corrosion rate are determined at every 50 hours of the test. It has been found that the corrosion resistance of the nano-modified specimens is improved in comparison with the one of the non-modified ones during the first fifty test hours of the cyclic immersion in both environments.

Keywords: nano-modified steel corrosion, nano-modifiers, GX120Mn12.

1. INTRODUCTION

The increased requirements to the fabricated metal products demand using metallic materials with improved properties for their production. Steels are the foundation of all construction and infrastructure facilities, automobiles, ships, tools and other industrial products. Until recently the properties of the steels are improved mainly by alloying with other elements or by selecting appropriate heat treatment modes.

One of the advanced techniques used to improve the properties of metallic materials during the last decade is the introduction of nano-sized particles of refractory compounds into the metal melts [1, 2]. It was found that modification with nano-sized particles results in a more uniform and homogeneous structure of metals. Depending on the type of nano-modifier the strength, ductility or wear resistance of the metals can be improved [3, 4].

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The impact of nano-modification on the mechanical properties of iron-carbon compounds is the subject of many studies [5, 6], but the published data from corrosion resistance tests of these alloys is still insufficient.

This paper presents the results from the corrosion resistance test of pieces of cast parts for excavation of aggregates from the riverbed made of either non-modified or nano-modified steel grade GX120Mn12 in different corrosive environments.

2. EXPERIMENTAL

2.1 Tested materials

Two types of specimens of steel GX120Mn12 are tested. The chemical composition of the steel is given in *Table 1*.

TABLE 1

No		Chemical composition [% wt]						
		C	Si	Mn	Cr	Ni	S	P
1	Steel GX120Mn12	$1.1 \div 1.3$	≤ 0.50	$11.5 \div 13.5$	≤ 1	–	0.02	0.01

The first type of specimens labeled with A are taken from parts made of Non-Modified (NM) steel and the second type of specimens labeled with B are taken from Modified Steel (MS) castings obtained in laboratory conditions in induction furnace at temperature 1530–1550 °C. The used Modifying Composition (MC) consists of 2 fractions TiCN + 1 fraction Y₂O₃ + 1 fraction Cr + 6 fractions Fe. TiCN and Y₂O₃ are nanoscale powders, Cr and Fe are micronized powders and serve as a plaque coating. The MC is introduced into the melt packed in aluminum foil and placed in a container. After the container melts the MC falls into the liquid metal. The homogenization of MC within the volume of the melt occurs in result of its convective motion induced by the electromagnetic field generated by the furnace inductor. The stirring of the metal during pouring from the furnace into the casting ladle contributes additionally for the homogenization too [7].

The total amount of the modifier is 0.025% by mass of the total steel composition. The composition of the modifier is selected to improve the mechanical properties of the material, such as hardness, strength and wear resistance.

Before cutting out the specimens the steel parts are subjected to heat treatment consisting in heating to 600 °C at a rate of 150 °C/h subsequent heating

from 600 °C to 1050–1080 °C at a rate of 200 °C/h, holding for 40 minutes, and quenching in water.

2.2. Test method

The accelerated model corrosion tests are carried out according to the method of cyclic immersion in corrosion medium and subsequent drying. The cyclic method is preferred to the usual continuous immersion because of the more aggressive corrosive effect of the medium due to the alternation of immersion and drying times.

To assess the impact of the corrosion environment on modified and non-modified steels, medium with different chemical compositions and corrosion aggressiveness is used. The compositions of the medium are chosen similar to the compositions of the working environments in which the parts actually operate. Medium No. 1 is an aqueous solution of NaCl, MgCl₂, and MgSO₄ (ground water), and medium No. 2 is a 3%NaCl solution. The main component of the two media are the chlorine ions (Cl⁻), but medium No. 1 is more aggressive because it contains both sulphate (SO₄²⁻) and chlor ions (Cl⁻).

The total duration of the test is 350 hours. The immersion/drying cycle is repeated with a preset frequency for a certain period of time. The ratio of the durations of immersion and drying is 1:2. During the test the air temperature is (27+1) °C, the temperature of the solutions is (25+1) °C, and the acidity of the solutions is pH = 5.5 and pH = 2 for medium No. 1 and No. 2, respectively. The mass loss Δm [g/m²] and the average corrosion rate K [g/m²h] of each test specimen are determined every 50 hours during the first 200 test hours.

Metallographic analysis of the steel structure GX120Mn12 in non-modified and nano-modified state before and after the corrosion tests is performed using optical microscope JENAVERT of Carl Zeiss.

3. RESULTS AND DISCUSSION

3.1. Microstructure of GX120Mn12 before the corrosion test

After the heat treatment the microstructure of the specimens of both modified and non-modified steel GX120Mn12 has austenitic structure with carbides deposited internally and along the grain boundaries. The size of the carbides in the non-modified steel is predominantly in the range from 3 μm to 50 μm, *Fig. 1(a, b)*. The size of the carbides in the modified steel is in the range from 3 μm to 40 μm, *Fig. 1(c, d)*, but carbides much larger in size (up to 15 μm) are also observed. Apart from the reduction of the average size of carbides, after

the modification some redistribution of the carbides in different grain areas is also observed. It should be noted that the larger carbides in the modified specimens are located on or near the grain boundaries, *Fig. 1(d)*.

Fig. 1. Initial structures of the tested specimens of steel GX120Mn12: (a) and (b) non-modified specimens (A); (c) and (d) modified specimens (B)

3.2 Results from the corrosion test

The results from corrosion tests of the modified and non-modified specimens are given in *Table 2*. The values for the mass loss Δm and the corrosion rate K are the arithmetic mean of three tested specimens of each type.

Figure 2 shows the change of corrosion rate K [g/m²h] with time for modified and non-modified steel specimens in both media.

The diagram shows that during the first 50-hours test period the corrosion rates of the non-modified specimens in both media are five times higher than

TABLE 2

Specimen No	After 50 hours		After 100 hours		After 150 hours		After 200 hours	
	Δm [g/m ²]	K [g/m ² h]	Δm [g/m ²]	K [g/m ² h]	Δm [g/m ²]	K [g/m ² h]	Δm [g/m ²]	K [g/m ² h]
A-1*	20.671	0.413	8.167	0.119	13.134	0.263	0.194	0.004
A-2*	17.340	0.346	5.978	0.119	4.498	0.089	13.460	0.269
B-1*	3.958	0.0790	6.112	0.1224	8.069	0.1614	7.065	0.1413
B-2*	3.286	0.0657	4.668	0.0367	6.414	0.1283	16.316	0.3273

* A and B mean non-modified and modified steel, accordingly, and 1 and 2 are the type of corrosion medium used.

Fig. 2. Corrosion rate during the test

those in the modified ones. The corrosion rate K in medium No. 1 is higher than in medium No. 2. The results for the non-modified specimens are similar, and the explanation is the higher concentration of the aggressive Cl^- and SO_4^{2-} ions in the solution. During this period of the test the surfaces of the samples are still clean, with no corrosion products formed and unlimited oxygen-to-metal access, which facilitates the corrosion process and increases the rate of corrosion.

The microscope observation of the corroded surfaces shows the presence of single unevenly distributed pits.

During the second 50-hours test period the corrosion rates of the non-modified specimens in both media are $2\div 2.5$ times lower than that during the first period due to the oxide layer formed on the surface of the specimens, which impedes the access of oxygen and the aggressive Cl^- and SO_4^{2-} ions from the solution and slows down the corrosion process.

The corrosion rate K of the modified specimen B-1 immersed in medium No. 1 is 1.5 times faster during the second period compared to the first period. However, for the modified specimen B-2 immersed in medium No. 2 the value of K is two times lower compared to the first period.

The data obtained for the third test period shows a sharp increase in the corrosion rate of the non-modified specimen (A-1) in medium No. 1 (ground water). The high value of the mass loss indicator gives evidence of active processes of general corrosion taking place.

In the modified samples an increase in the rate of corrosion in both media is observed as a consequence of the experimental conditions: a sequential impact of the aggressive ions in the solutions and of the oxygen in the air. The pits observed initially are increased in size and merged, and the corrosion layer covers the entire surface.

The data obtained for the fourth period of the study shows that corrosion rate of sample B-1 (modified in ground water) remains almost unchanged after the previous period, and the value of K of sample A-1 (non-modified) is close to zero, which means that the corrosion process slows down. The reason for attenuation is the formation of a dense layer of corrosion products during the third period, which impedes the access of the aggressive ions from the solution to the metal surface.

During the fourth period there is a sharp increase in the corrosion rate K of both types of specimens in medium No. 2 (3%NaCl).

3.3. Visual corrosion analysis after 350 hours of test

Figure 3 shows the corroded surfaces of the samples after 350 hours of cyclic corrosion testing. It is obvious that the accumulated corrosion products have multiple layers with different morphology in all specimens.

The observed corrosion products have colours that are typical for oxidized iron (Fe^{3+}), from lemon yellow, through light- and reddish brown, to dark brown. Some greenish-brown deposits are also observed. These are the colours of $\alpha\text{-FeOOH}$ (goethite), $\beta\text{-FeOOH}$, $\gamma\text{-FeOOH}$ (lepidocrocite), $\alpha\text{-Fe}_2\text{O}_3$ (hematite) [8, 9], and that assumption is confirmed by the X-ray diffraction analysis of the corrosion product. The reason for the formation of corrosion compounds is the easy oxidation of Fe^{2+} to Fe^{3+} in aqueous solution under

Fig. 3. Corrosion products deposited on the surfaces of test specimens after 350 test hours: (a) corrosive surface of non-modified specimens, medium No. 1 (ground water); (b) medium No. 2 (3%NaCl); (c) corrosive surface of modified specimens, medium No. 1 (ground water); (d) medium No. 2 (3%NaCl)

the influence of dissolved oxygen from the air. The formation of iron oxides and hydroxides is influenced by the presence of additional cations and anions in the solution.

The greenish-brown deposits observed in some areas of the surface and between the layers are the so-called “green rust”. These are hydrated colored iron compounds containing Cl^- , SO_4^{2-} or CO_3^{2-} ions, which are formed in highly humid environments with access of oxygen. The “green rust” is a transition phase and after subsequent oxidation transforms into the more stable phases $\alpha\text{-FeOOH}$ and Fe_3O_4 .

The accumulation of corrosion products on the surfaces of the specimens and the amount of iron added by means of the nano-modifier are some of the

reasons for the change in corrosion rate over the later test periods. On the other hand, it is known that the addition of Cr enhances the susceptibility to intercrystalline corrosion, and Cr is one of the elements in the composition of the nanomodifier used [10]. There is evidence for the influence of Y_2O_3 on the corrosion behavior of this type of steel. It is known that Y_2O_3 increases the corrosion resistance and prevents the rapid corrosion attack in aggressive environment [2, 3]. The improved corrosion resistance of specimens coated with Y_2O_3 is due to the formation of the complex compound FeY_2O_4 , which acts as a grain boundary barrier and prevents the migration of cations and anions [11]. It has been found that the increased percentage of TiCN significantly stimulates the corrosion process [12].

Fig. 4. Development of intergranular corrosion after 350 hours of corrosion test: (a) non-modified specimens, medium No. 1 (ground water); (b) medium No. 2 (3%NaCl); (c) modified specimens, medium No. 1 (ground water); (d) medium No. 2 (3%NaCl)

The metallographic study found evidence of intergranular corrosion in both modified and non-modified specimens after the corrosion test in both media. In the modified specimens, the intergranular corrosion occurs at an earlier test stage, i.e. after the 250th hour, and in the non-modified ones it occurs after the 300th to 350th hour. In the specimens immersed in medium No. 1 (ground water) the intergranular corrosion is better expressed, *Fig. 4(a, c)*, whereas in the specimens immersed in medium No. 2 (3%NaCl) it is less pronounced, *Fig. 4(b, d)*. The results for the non-modified specimens are similar but here the intergranular corrosion covers smaller areas, *Fig. 4(a, b)*.

The occurrence and development of intergranular corrosion is typical for steels undergone structural changes, e.g. separation of new phases along the grain boundaries. In addition to the structural refinement after modification of steel GX120Mn12, increased amount of chromium carbides along the grain boundaries and reduced concentration of C and Cr in the surrounding areas are also observed during the present study. The further growth of the Cr-carbides takes place on account of C from the solid solution, and only the Cr around the boundaries participates in the carbide reaction. This is the reason for the appearance of Cr-depleted areas around the grain boundaries and hence the reduction of corrosion resistance, which results in appearance of intergranular corrosion.

4. CONCLUSION

- The data on the development of corrosion process in both non-modified and nano-modified specimens of steel grade GX120Mn12 obtained by determining the indicators for the mass loss and the average corrosion rate shows improved corrosion resistance of the nano-modified specimens during the initial test periods, i.e. the first one hundred hours.
- After one hundred hours of cyclic corrosion test the specimens of steel GX120Mn12 modified with 0.25% composition of TiCN + Y₂O₃ + Cr + Fe in proportion 2:1:1:6 show a greater susceptibility to development of intergranular corrosion compared to the specimens of non-modified steel in both media (ground water and 3%NaCl).
- The modifier TiCN+Y₂O₃+Cr+Fe in proportion 2:1:1:6 introduced to improve the mechanical properties of steel grade GX120Mn12 has not a positive impact on its corrosion resistance.

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СРАВНИТЕЛНО ИЗСЛЕДВАНЕ НА КОРОЗИОННАТА УСТОЙЧИВОСТ НА ОБРАЗЦИ ОТ НЕМОДИФИЦИРАНА И НАНОМОДИФИЦИРАНА СТОМАНА GX120Mn12

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Резюме. Изследвано е корозионното поведение на образци от стомана GX120Mn12 преди и след нейното модифициране посредством модификатор със състав $TiCN + Y_2O_3 + Cr + Fe$ в съотношение 2:1:1:6. Използван е методът на циклично потапяне в среди с различна агресивност – разтвор на NaCl, $MgCl_2$ и $MgSO_4$ и 3%NaCl. Определени са показателите – загуба на маса и средна скорост на корозия, на всеки 50 часа от изпитването. Установено е, че корозионната устойчивост на модифицираните образци е подобрена в сравнение с тази на немодифицираните такива при първите петдесет часа от изследването на циклично потапяне и в двете среди.

Ключови думи: корозия на наномодифицирана стомана, наномодификатори, GX120Mn12.

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