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Influence of carbon on the structural-phase composition and hardness of steel ingots of the Fe-Cr-Mo-N-C system obtained by the SHS method under nitrogen pressure

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The possibility of obtaining solid ingots (without gas porosity in the volume) from high-nitrogen steel of the Fe-Cr-Mo-N-C system by the method of self-propagating high-temperature synthesis under nitrogen pressure is shown in the present paper. It has been established that with an increase in the mass fraction of carbon from 0.09% to 0.30% in the as-cast metal, the hardness of the metal increases. At the same time, the structural-phase composition consists of a pseudo-pearlitic structure (ferrite-nitride mixture) and austenitic structure in different ratios since an increase in the carbon content leads to an increase in the amount of the pseudo-pearlite. The heat treatment of specimens with a mass fraction of carbon of 0.09% and 0.30% at 1250°C for two hours leads to their complete austenization. In this case, the hardness of steels of both compositions decreases to 22 – 24 HRC (0.09 wt.% of carbon) and to 28 – 30 HRC (0.30 wt.% of carbon).

Keywords: high-nitrogen corrosion-resistant steel, aluminothermy under nitrogen pressure, structural-phase composition.

1. Introduction

At present, materials resistant to specific types of corrosion, for example, pitting corrosion, are of particular interest in industry [1,2]. Pitting is a form of corrosion that leads to the random formation of small holes in the metal surface. Pitting is very destructive for a metal item because pits can perforate the metal. This type of corrosion is more often observed in media with a high content of chlorides at elevated temperatures [3].

One of the most promising ways to prevent pitting corrosion is the rational choice of a corrosion-resistant alloy for the production of a required item. The resistance of an alloy to pitting resistance can be assessed by calculating the so-called Pitting-Resistance-Equivalent-Number (PREN index) based on the chemical composition of the material [3,4]:

$$\mathrm{PREN} = \%\mathrm{Cr} + 3.3 \cdot \%\mathrm{Mo} + x \cdot \%\mathrm{N}, \qquad (1)$$

where x takes values from 13 to 30.

According to [3,4], for steels containing up to 4.5 wt.% of molybdenum x=16 and for steels with the molybdenum content of 4.5 – 7.0 wt.% x=30. In accordance with [5,6] it should be noted that chromium, molybdenum, carbon and nitrogen (in the solid solution) increase corrosion resistance, and according to [6] manganese and nickel decreases it to a certain extent. In [6,7] it is proposed to use the MARC index (measure of alloying for ensuring corrosion resistance) instead of the PREN index:

$$\begin{aligned} \mathrm{MARC} = \%\mathrm{Cr} + 3.3 \cdot \%\mathrm{Mo} + 20 \cdot \%\mathrm{N} + \\ + 20 \cdot \%\mathrm{C} - 0.5 \cdot \%\mathrm{Mn} - 0.25 \cdot \%\mathrm{Ni}. \end{aligned} \qquad (2)$$

In the relation for the MARC index, the combination of carbon and nitrogen is considered as a factor positively influencing the corrosion resistance, and nickel and manganese — as a negatively influencing factor [5]. At present, a promising trend is the development of compositions and technologies for obtaining and treatment of corrosion-resistant high-nitrogen steels (HNSs) [8,9]. However, the production of such steels containing ferrite-forming molybdenum without alloying with manganese and nickel presents a number of serious difficulties. One of the ways to overcome the difficulties is the use of the method of self-propagating high-temperature synthesis (SHS) under nitrogen pressure [10 – 12]. The SHS-metallurgy is more economically feasible for obtaining steels with the over-equilibrium nitrogen content [10 – 13]. However, despite a number of obvious advantages of the SHS-metallurgy, the high speed of the reaction makes the aluminothermic process poorly-controlled. Therefore, for obtaining steel ingots of the specified composition and good quality, thorough development of the technical regimes of production is required.

In [13, 14], the possibility of obtaining nickel-free HNSs by SHS is shown. In [11,12], it is demonstrated that nickel- and manganese-free HNSs of the system Fe-Cr-N can be obtained by the SHS method. Further investigation of the processes of the production of nickel- and manganese-free HNSs of the system Fe-Cr-N additionally alloyed with molybdenum and carbon by the SHS-metallurgy method is promising for obtaining sparingly-alloyed steels resistant to pitting corrosion in connection with the relations for PREN and MARC indices. The evaluation of the influence of different carbon content on the strength and corrosion-resistance properties of steel containing chromium, molybdenum and nitrogen in overequilibrium concentration is of special interest. On the one hand, an increase in the carbon content leads to the increase of the values of the strength characteristics [15,16] and temperature of the pitting formation in accordance with the relation for the MARC index. On the other hand, in [17] it is noted that with an increase in the carbon content the steel corrosion resistance decreases due to the tendency toward the formation of carbides of the $Me_{23}C_6$ type. Thus, in austenitic nitrogen-containing steels, carbon can simultaneously positively influence the strength and corrosion resistance properties only when it is completely dissolved in austenite (homogeneous austenitic structure). In [18] it is noted that the combined alloying of steel with carbon and nitrogen can lead to the improvement of its strength, viscosity and ductility and ensures the preservation of sufficiently high corrosion resistance (for example, steel with the total mass fraction of carbon and nitrogen from 0.85 to 1.0%). However, in the literature there is no information about the effect of different carbon content on steel with the mass fraction of chromium from 21.0 to 23.5%, molybdenum from 2.0 to 2.3% and nitrogen from 1.15 to 1.20%.

When steel has a homogeneous austenitic structure, it is possible to evaluate the effect of different carbon content on the steel strength characteristics by measuring hardness, and the carbon content effect on pitting corrosion can be evaluated by the MARC index calculation [5].

Thus, the purpose of the present paper is to find the possibility of obtaining a homogeneous austenitic structure in ingots from steels containing the mass fraction of chromium from 21.0% to 23.5%, molybdenum from 2.0% to 2.3% and nitrogen from 1.15% to 1.20% produced by SHS under nitrogen pressure at different carbon content and the MARC index value more than 50. Additionally, the possibility of determining the influence of different carbon content on the hardness of the above steels is studied.

2. Specimen preparation and investigation methods

In the present paper, to study the possibility of obtaining HNSs alloyed with molybdenum, which do not contain nickel and manganese for providing sufficient pitting resistance at lean alloying, the HNSs of the system Fe-Cr-Mo-N-C were chosen as investigation objects. The chemical composition of the steels is given in Table 1. The steel ingots were prepared by metallothermic reduction of oxides in a nitrogen atmosphere at high pressure in the SHS regime. When the chemical composition indicated in Table 1 was selected, it was taken into consideration that different carbon contents would allow to reveal the regularities of the carbon effect on the structure and properties of the metal of the studied HNS ingots and carbon would provide the steel sufficient resistance to pitting and general corrosion ($MARC_{max} = 61.49$ and $MARC_{min} = 52.20$; $PREN_{max} = 50.29$ and $PREN_{min} = 46.00$).

For the experimental melting by aluminothermy under nitrogen pressure, the mixtures were prepared with the use of the following materials as reagents: the powders of p. a. (Pro Analysi) grade iron oxide Fe_2O_3 TU 6-09-5346-87, OHM-0 grade chromium oxide Cr_2O_3 GOST 2912-79 and pur. (Purum) grade molybdenum oxide MoO_3 TU 6-09-4471-77; PAM-4 grade aluminum-magnesium powder GOST 5593-78 or ASD-1 grade aluminum powder TU 1791-99-019-98; chromium nitride obtained as a result of nitriding of PH-1M grade chromium powder TU 14-1-1474-75 by SHS. To remove moist and to increase the specific surface, the mixture oxide components were preliminary dried in an electric furnace at 250°C for 1–2 h and ground in a ball mill. The weighed mixture components were processed in a mixer. The aluminothermic synthesis of the HNSs was performed in a SHS-reactor RVS-10 under nitrogen pressure up to 15 MPa. The HNS synthesis was conducted according to the procedure described in [10–12].

The synthesis product was metal ingots with an easily separated layer of slag on the upper part. The obtained ingots weighed 156–160 g. Table 2 presents the results of the chemical analysis of the ingots, which satisfy the requirements to the chemical composition given in Table 1, and the PREN and MARC indices calculated for the ingots.

The specimens for the investigation were prepared by the spark cutting of the ingots.

The ingot metal was investigated both in the as-cast state and after thermal treatment (holding at 1250°C for 2 h followed by water quenching).

The gas analysis for determining the nitrogen content in the specimens was performed on an analyzer Metavac-AK by the method of reduction melting in a helium atmosphere using a katharometer as a detector.

The chemical analysis for determining the content of metals in the specimens was performed on an atomic emission spectrometer Spectroflame Modula S.

Metallographic investigations were conducted on a microscope NEOPHOT-21 after the sections of the metal prepared from the ingots in the as-cast state were etched in Marble's reagent consisting of 4 g of $CuSO_4$ in 20 ml of HCl and 20 ml of H_2O and the sections of the metal of

Table 1. Selected chemical compositions of the studied ingots, wt.%.

Fe	Cr	Mo	N	C
Base	21.0–23.5	2.0–2.3	1.15–1.20	0.08–0.12
				0.28–0.32

Table 2. Chemical composition of the obtained ingots and their PREN and MARC indices.

No.	PREN	MARC	The chemical composition of the obtained ingots, wt.%				
			Fe	Cr	Mo	N	C
1	47.44	53.96	Base	21.3	2.2	1.18	0.09
2	48.98	59.70	Base	23.5	2.0	1.18	0.30

the thermally treated ingots were etched in the solution of concentrated nitric and hydrochloric acids (10 ml of HNO_3 and 30 ml of HCl). X-ray phase analysis was performed on a diffractometer DRON-6 (CoK_α-radiation, graphite used as monochromator).

Hardness was determined by the Rockwell method performed on a ITBRV-187.5-AM tester according to GOST 9013-59.

The resistance to pitting corrosion was determined by the chemical method according to GOST 9.912-89. Small samples were used for testing. The average conditional pitting corrosion rate (V_m) was a criterion for resistance to pitting corrosion.

3. Results and discussion

Figure 1 shows the diffraction pattern of a specimen cut from ingot No. 1 in the as-cast state containing 0.09 wt.% of carbon. The analysis of the diffraction pattern shows the presence of ferrite and austenite in the ratio 1/9, respectively (see Fig. 1: the peaks related to ferrite are indicated by rhombi and the austenite peaks — by circles).

The microstructure of the specimen prepared from as-cast ingot No. 1 (Fig. 2) consists of austenite (up to 90%) and pseudo-pearlite (ferrite-nitride mixture) in the amount of up to 10%. As a result of hardness measurement it is established that the hardness of the specimen cut from as-cast ingot No. 1 is 30 – 32 HRC.

An increase in the mass fraction of carbon to 0.30% (ingot No. 2) leads to a change in the ratio of ferrite/austenite, which becomes 9/16, respectively (in Fig. 3, on the diffraction pattern the ferrite peaks are indicated by rhombi and the austenite peaks — by circles).

The microstructure of the specimen prepared from as-cast ingot No. 2 in Fig. 4 is a pseudo-pearlitic structure consisting of a ferrite-nitride mixture (up to 36%) and an austenitic structure (up to 64%). As a result of hardness measurement it is established that the hardness of the specimen cut from as-cast ingot No. 2 is 40 – 43 HRC.

The metallographic investigations and visual control show the absence of gas porosity in the obtained ingots.

Thus, the investigation results show that by using the aluminothermic method it is possible to obtain solid ingots (without gas porosity in the volume) of HNSs of the Fe-Cr-Mo-N-C system with the mass fraction of nitrogen 1.18% at the carbon content 0.09 wt.% and 0.30 wt.%.

In steels of the Fe-Cr-Mo-N-C system of the selected compositions, with the same nitrogen mass fraction the as-cast-metal hardness increases with an increase in the carbon content. This is most likely due to the difference in the structural-phase composition of the ingots. In the steel of the considered system, an increase in the carbon mass fraction from 0.09% to 0.30% leads to an increase in the fraction of the pseudo-pearlitic structure (from 10% to 36%) consisting of finely dispersed ferrite-nitride mixture. Figure 5 presents a magnified image of a typical pseudo-pearlitic structure which is observed as dark areas on the microsections at higher magnification (Figs. 2 and 4). A similar pseudo-pearlitic structure is described in [10]. In addition, it is known from the literature [18] that similarly to nitrogen, carbon, which is

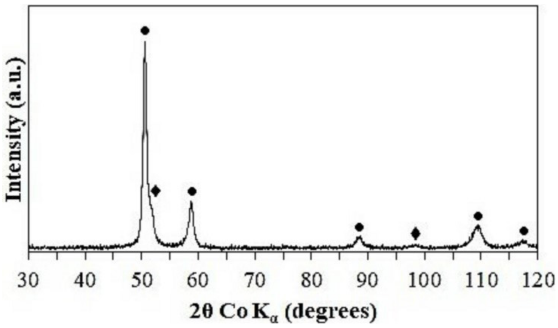

Fig. 1. The XRD pattern of a specimen cut from ingot No. 1 in the as-cast state containing 0.09 wt.% of carbon: the peaks related to ferrite are indicated by rhombi and the austenite peaks — by circles.

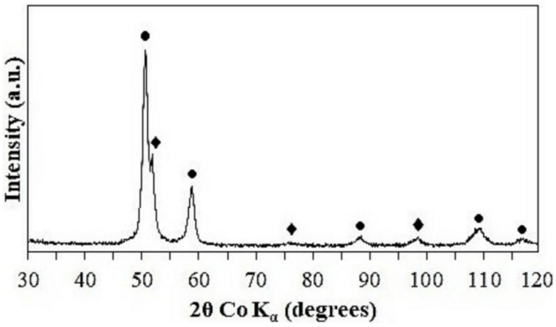

Fig. 3. XRD pattern for the specimen cut from as-cast ingot No. 2 containing 0.30 wt.% of carbon: the ferrite peaks are indicated by rhombi and the austenite peaks — by circles.

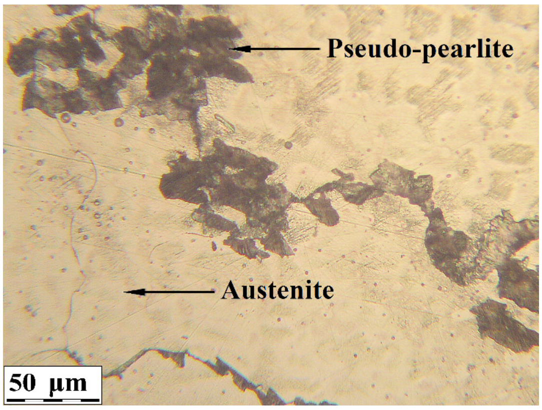

Fig. 2. (Color online) Microstructure of the specimen cut from as-cast ingot No. 1 containing 0.09 wt.% of carbon.

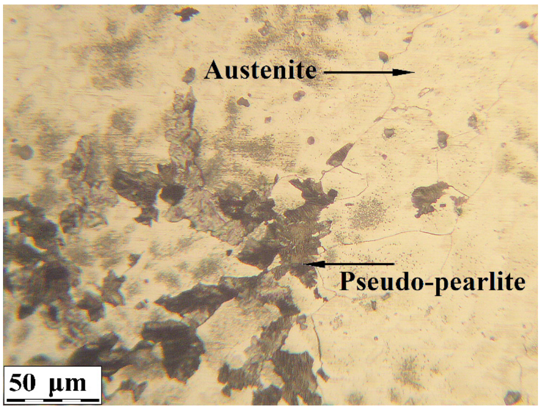

Fig. 4. (Color online) Microstructure of the specimen cut from ingot No. 2 in the as-cast state containing 0.30 wt.% of carbon.

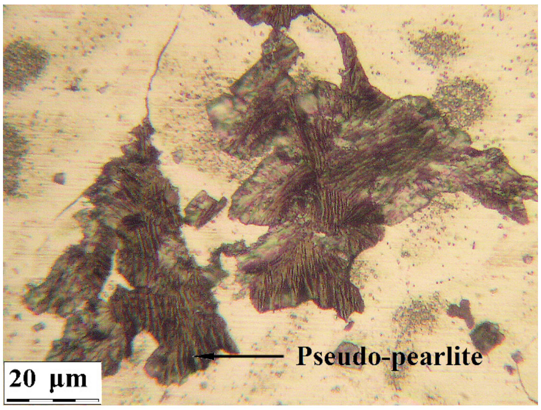

Fig. 5. (Color online) Typical image of the pseudo-pearlitic structure of the metal of the ingots prepared from the high-nitrogen steels of the Fe-Cr-Mo-N-C system.

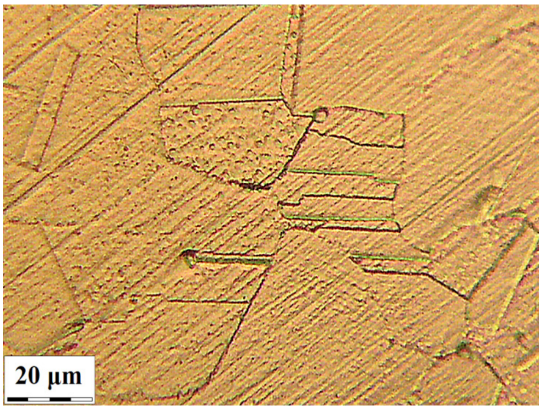

Fig. 8. (Color online) Typical image of the microstructure of the specimens prepared from ingots No. 1 and No. 2 after heat treatment.

a typical interstitial element, hardens the ingot austenite in iron-based alloys during alloying.

After the thermal treatment of the specimens cut from ingots No. 1 and No. 2 at 1250°C for 2 h followed by water quenching, the only phase — austenite — is observed on the XRD patterns (Figs. 6 and 7, respectively).

The microstructure of the quenched specimens cut from ingots No. 1 and No. 2 is typical for the austenite of corrosion-resistant steel (Fig. 8). The hardness measurements show that the specimen with the carbon mass fraction 0.30% has higher hardness (28 – 30 HRC) than the specimen with the carbon mass fraction 0.09% (22 – 24 HRC). According to the existing literature data [15,16,17], this can be explained by that being an interstitial element, carbon influences austenite: the higher carbon concentration is, the more hardening effect on austenite it produces, and in this case, the steel hardness increases.

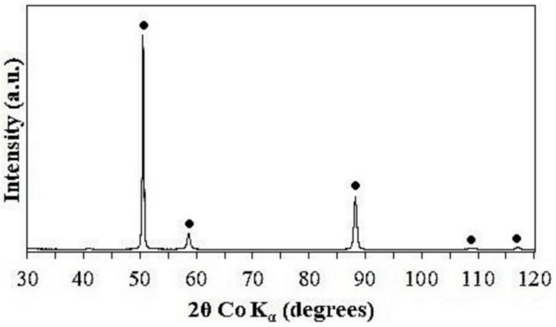

Fig. 6. XRD pattern of the specimen prepared from ingot No. 1 in the quenched state with 0.09 wt.% carbon: the austenite peaks are indicated by circles.

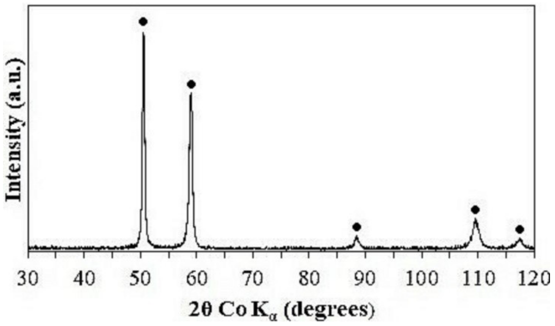

Fig. 7. XRD pattern of the specimen cut from ingot No. 2 in the quenched state with 0.30 wt.% carbon: the austenite peaks are indicated by circles.

The decrease in the hardness of the specimens prepared from ingots No. 1 and No. 2 observed after thermal treatment at 1250°C for 2 can be due to the revealed change of their phase composition. Based on the obtained results it can be concluded that the presence of the pseudo-pearlitic structure significantly increases hardness. The combined effect of different content of carbon and the pseudo-pearlitic structure on the change of hardness as a result of thermal treatment can be formulated as follows: the lower the content of the carbon and pseudo-pearlitic structure is in the as-cast steel specimen, the smaller decrease of the specimen hardness is after thermal treatment with holding at the homogenizing temperature.

Based on the calculation results for the PREN and MARC indices (Table 2) and taking into consideration that it is possible to obtain a completely austenitic structure after the thermal treatment of the steels of the Fe-Cr-Mo-N-C system with the carbon mass fraction 0.09% and 0.30%, it can be concluded that the chemical composition of the steels in Table 2 potentially provide satisfactory resistance to pitting and general corrosion. It also can be concluded that steel with the carbon content 0.30% has potentially higher resistance to pitting corrosion.

The calculated PREN index for both compositions (see Table 2) is more than 40, which indicates a potential possibility of the use of parts made of the given steels for operations in media with a higher content of chloride ions.

Moreover, tests have shown that samples of both compositions are resistant to pitting corrosion. The total mass loss of parallel samples did not exceed twice the error of their weighing ($V_m \approx 0$ g/cm$^2 \cdot$h).

4. Conclusions

1. Solid ingots (without gas porosity in the volume) of the high-nitrogen steel of the Fe-Cr-Mo-N-C system were obtained by aluminothermy.

2. The microstructure of the ingots of the HNS of the Fe-Cr-Mo-N-C system with the carbon mass fraction of both 0.09% and 0.30% consists of a pseudo-pearlitic structure (ferrite-nitride mixture) and an austenitic structure in

different ratios, namely: 10% of the pseudo-pearlitic structure and 90% of the austenitic structure at the carbon mass fraction 0.09%, and at 0.30% of carbon — 36% of the pseudo-pearlitic structure and 64% of the austenitic structure.

3. It is established that in the HNS of the system Fe-Cr-Mo-N-C at the nitrogen fraction 1.18% an increase in the carbon mass fraction from 0.09% to 0.30% leads to an increase in the ingot metal hardness from 30–32 HRC to 40–43 HRC.

4. Heat treatment of specimens of the HNS of the Fe-Cr-Mo-N-C system with a carbon mass fraction of 0.09% and 0.30% at 1250°C for 2 h followed by water quenching leads to complete austenization of the steel. In this case, the hardness of steels of both compositions decreases: at a carbon mass fraction of 0.09% — to 22–24 HRC and at a carbon mass fraction of 0.30% — to 28–30 HRC.

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