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Conference Paper

Study of the Process of Alloying Steel By Nitrated Chromium

Leonid Andreevich Smirnov¹, Oleg Vadimovich Zayakin¹, Vladimir Ivanovich Zhuchkov¹, Alexey Sergeevich Oryshchenko², and Grigoriy Yurievich Kalinin²

Abstract

Experimental investigation of process of steel alloying by nitrated chromium was carried out. As raw material for metal-melt treatment, the steel containing 20.3% Cr; 11.2% Mn; 7.1% Ni; 1.46% Mo; 0.33% Si; and 0.05% C was used. As-cast samples of nitrated chromium (ΦΧΗ10 and ΦΧΗ20 grades) were used as alloying additives. The compositions of grades are 85.7% Cr; 8.0% N, and 73.9% Cr; 16.1% N, respectively. Experiments were carried out in high-temperature laboratory unit at 1500°C. It was found that the degree of nitrogen transfer into steel reaches up to 84% at the application of as-cast specimen of nitrated chromium containing 8% of nitrogen and 1 min exposure time after addition to ferroalloy. Further high-temperature soaking of nitrated steel causes a dropdown of nitrogen concentration due to thermal dissociation of existed nitrogen-containing compounds in the melt and exhalation in gas phase. This prevents nitrogen transfer into the steel. It was demonstrated a possibility in principle of obtaining of chrome-manganese steel containing about 0.4–0.6% of nitrogen at melt alloying by nitrated chromium in air atmosphere at exposure time up to 15 min.

Keywords: metallurgy, nitrogen, chromium, steel, digestion degree, physicochemical characteristics

1. Introduction

Nitration of steels enables one to decrease its prime cost due to lower consumption of costly ferroalloys and improve functional properties of steel products. Addition of nitrogen leads to improvement of strength, ductility, and corrosion-resistance of austenite steels [1]. Currently, nitrogen doping is used in the preparation of various grades of general purpose steels - from stainless to low-alloyed [2–9] and micro-alloyed for construction and engineering [10–12]. Nitrated ferroalloys are used for the production of steels with high content of nitrogen. Alloying by nitrogen enables one to decrease a content of nickel and manganese in steels. The price of alloying elements has a significant impact on the prime cost of corrosion-resistant steels grades. Well-known grades of nitrated ferroalloys FeMn80C05N2 (1.5–2.5% N), FeMn70C10N5 (4–8% N), ΦXH100–ΦXH600 (1–6% N) and new ones with increased nitrogen content (ΦXH10, ΦXH20 – 8–20% N, respectively), as well as Nitrovan12 and Nitrovan16 [16] are used in state-of-the-

Corresponding Author:
Oleg Vadimovich Zayakin
zferro@mail.ru

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¹Institute of Metallurgy UrD RAS, Ekaterinburg, Russia

²CRISM Prometey of NRC Kurchatov Institute, St. Petersburg, Russia



art conditions of steel making. For efficient application of new ferroalloys compositions the knowledge of their functional characteristics [16–18] and features of steel alloying processes proceeding [19–20] are highly demanded.

In the present work the nitrated chromium (Φ XH10, Φ XH20 grades) were chosen as the samples for studying of steel nitration process. Chemical composition of initial samples is listed in the Table. Φ XH10 and Φ XH20 specimens were obtained by melting and sintering, respectively. The steel (Φ 4X20H6 Γ 11M2A Φ 5 grade) was used for treatment as metal melt.

Sample Chemical Concentration*, % С Cr Р S Si Mn ΑI Ferroalloy ФXH10 0.21 85.7 0.007 0.011 0.11 4.02 Ferroalloy ФХН20 0.13 73.9 no data 0.015 0.55 0.35 0.05 20.3 11.2 0.014 0.006 0.33 04Х20Н6Г11М2АФБ Ti Sample Ν Ni Мо V Nb Ferroalloy ФХН10 8.00 Ferroalloy ФXH20 16.05 0.05 7.1 0.19 0.037 Steel 1.46 0.15 04Х20Н6Г11М2АФБ

TABLE 1: Chemical composition of initial samples.

Note: *Iron and other admixtures to the balance.

Source: Author's own work.

Studying of process characteristics of steel alloying by nitrated chromium was carried out in laboratory conditions using Tamman furnace with protecting cover in air. Experiments were carried out at temperature 1500 °C. Nitrated chromium was added to the steel melt and exposure of the melt was up to 30 min, during this period sampling was carried out. The added quantity of nitrated chromium was made according to calculated value of nitrogen to obtain its 1% concentration. At the stage of ferroalloy addition there were the two processes 1) nitration and 2) alloying by appropriate elements. Chromium content was increased in the steel up to \sim 28.5 and 24.7% at application of Φ XH10 and Φ XH20, respectively, and it was nearly constant during exposure time.

Kinetic curves of nitrogen content in steel with exposure time are presented in Figure 1. Relationship between exposure time and nitrogen transfer degree is shown in Figure 2.

The result obtained using as-cast sample of nitrated chromium (8% N) is by far the best concerning nitrogen content and its transfer degree. At temperature 1500 °C and exposure time 1 min after alloying the digestion degree was 84% (at nitrogen content in steel 0.84%), while exposure time was 30 min the digestion degree became only 52%



(N concentration in steel 0.52). It is necessary to note that the sharp drop of nitrogen content from 0.84 to 0.62 was during first period of exposure (5 min). Three kinetic regions of nitrogen behavior may be marked out at the curves (Figure 1). First, nitrogen absorption by the melt; second, nitrogen desorption with high rate; third, low rate desorption (approaching of equilibrium state). The values of nitrogen concentration in steel in first minutes after alloying is above equilibrium one. There is the explanation of further decrease of nitrogen content during 30 min exposure. The short-term high nitrogen content in the steel can be explained by the form of its entry into the melt. X-ray diffraction analysis of ferroalloys revealed that Φ XH10 sample consists of \sim 80% Cr_2N and \sim 20% solid solution of iron in chromium. As for Φ XH20 alloy, there was detected two types of chromium nitrides CrN and $(CrFe)_2N$, their ratio (between each other) was about 4:1. Nitrogen releases in gaseous phase from nitrated steel samples at high-temperature exposure due to thermal dissociation of nitrogen-containing compounds. Besides, the higher content of nitrogen in steel is, the higher intensity of its release.

The nitrogen digestion degree is strongly dependent on properties of chromium, manganese and other elements nitrides formed in the steel, temperature, and characteristics of used alloys: type of nitrogen compounds in nitrated ferroalloy and alloy microstructure (density, porosity). True and apparent density of ferroalloys under investigation was measured by picnometric technique. It was found that an increase of nitrogen content in ferrochrome (in the considered range) leads to decrease of its true density. This enables one to obtain alloys characterized by optimal values of density 6200–6700 kg/m³. However, they have very low apparent density values due to very high porosity of nitrated ferroalloys: ΦXH10 – 4170 kg/m³ and ΦXH20 – 3540 kg/m³. Due to the lower density, the ΦXH20 alloy can more melt on the surface of the steel melt and is characterized by a lower degree of nitrogen absorption into the steel compared to the more dense ΦXH10 alloy. It seems logical to conclude that ΦXH20 alloy with lower density will be more melted at the surface of steel melt.

It seems that the higher nitrogen digestion degree at application of Φ XH10 is due to alloy cast structure (higher density) and the lowest nitrogen content on the chromium unit (N/Cr in the alloy is 0.09), while the N/C ratio is 0.22 in Φ XH20 alloy.

Obtained experimental data concerning nitrogen transfer degree (38–55%) from the ferroalloys under investigation into steel at 15 min. exposure time corresponds to the literature data. In the research [21] it was demonstrated that at steel alloying by nitrated vanadium and ferromanganese with 4–8% N in a bucket, the nitrogen digestion degree is 55–65 and 20–35%, respectively.

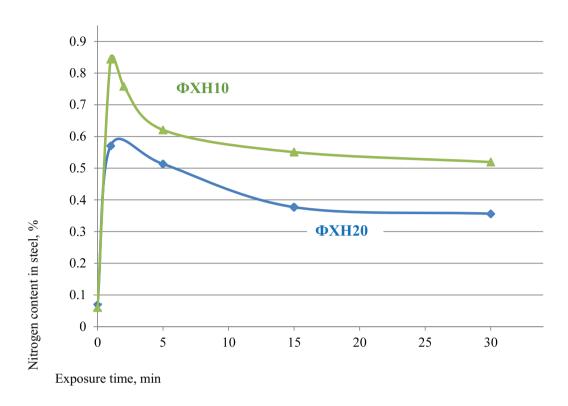


Figure 1: Time-temperature dependence of nitrogen content in steel at alloying by nitrated chromium at 1500°C.

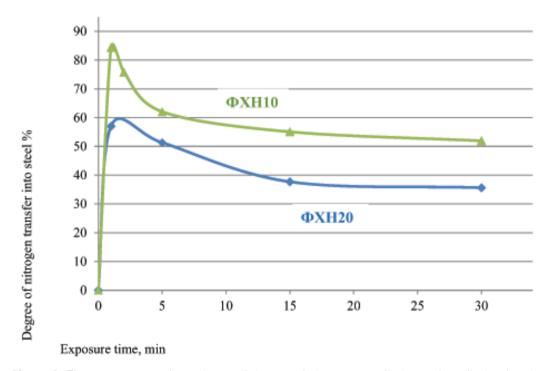


Figure 2: Time-temperature dependence of degree of nitrogen transfer in steel at alloying by nitrated chromium at 1500°C.



2. Conclusions

- 1. The experimental time-temperature dependence of nitrogen distribution at alloying of steel (04Χ20H6Γ11M2AΦ5 grade) by as-cast ΦΧH10 and sintered ΦΧH20 ferrochromium was studied at 30 min exposure time in light-oxidizing atmosphere at 1500°C.
- 2. It was found that the highest transfer degree of nitrogen in steel is 84%. It was detected at application of as-cast nitrated chromium sample having 8% of nitrogen and short exposure time (1 min) after ferroalloy addition. Further high-temperature soaking of nitrated steel causes a drop down of nitrogen concentration due to thermal dissociation of existed in the melt nitrogen-containing compounds and exhalation in gas phase. This prevents nitrogen transfer into the steel.
- 3. It was demonstrated a possibility in principle of obtaining of chrome-manganese steel containing 0.4–0.6% of nitrogen at melt alloying by nitrated chromium in air atmosphere at exposure time up to 15 min.

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