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Nitrided Ferroalloy Production By Metallurgical SHS Process: Scientific Foundations and Technology

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Abstract

The main objective of this paper is to present results of the research in the development of a specialized self-propagating high-temperature synthesis (SHS) technology for ferroalloy composites, as applied to steelmaking. The problem of creating such a production cycle has been solved by developing a new approach to the practical implementation of self-propagating high-temperature synthesis, as applied to metallurgy. The metallurgical variation of SHS is based on the use of different metallurgic alloys (including waste in the form of dust from ferroalloy production) as basic raw materials in the new process. Here, the process of synthesis by combustion is realized through exothermic exchange reactions. The process produces a composite, based on inorganic compositions with a bond of iron and/or alloy based on iron. It has been shown that in terms of the aggregate state of initial reagents, metallurgical SHS processes are either gasless or gas-absorbing. Combustion regimes significantly differ when realized in practice. To organize the metallurgical SHS process in weakly exothermic systems, different variations of the thermal trimming principle are used. In the present study, self-propagating high-temperature synthesis of ferrovanadium nitride, ferrochromium nitride and ferrosilicon nitride; which is widely used in steel alloying, was investigated.

Keywords: self-propagating high-temperature synthesis (SHS); composite ferroalloys; nitrides; borides; filtration combustion; ferrovanadium nitride ferrochromium nitride and ferrosilicon nitride

Nitrogen has been widely used as a alloying element since World War II as it proved to be an effective substitute for nickel in stainless steels. Nitrogen stabilizes austenite and strengthens the austenite matrix. The austenite-promoting effect of nitrogen is 20 times stronger than that one of nickel. At that, unlike carbon that also greatly expands the gamma field, nitrogen increases resistance to corrosion. At present, the metallurgical industry has mastered doping of 16G2AF high-strength low-alloyed steel with nitrogen. Finely dispersed vanadium nitrides and carbonitrides in such steels improve the

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Page 191

steel strength by $\sim$ 20% (and more) as compared to regular low-alloy steels of 09G2S and 14G2 grades. The nitrogen microalloying is also effectively used in smelting grain-oriented steel with nitride inhibition. Today, nitrogen-bearing steels find application in power engineering, engine manufacturing, chemical engineering and other industries, and boron-alloyed steels are indispensable to nuclear power industry. Microadditives of nitrogen and boron have also become useful in steel production.

Nitrogen naturally occurs mainly in gaseous form; therefore, to introduce it into steel, it needs to be bound in solid matter. Such nitrogen-containing materials must be compatible with the molten steel and adaptable to specific process conditions. That is why nitrided ferroalloys and metals commonly serve as a source of nitrogen. Advantageously, the technology of nitriding steel with alloys is universally applicable, and such master alloys can be used in all types of steel-making units at metallurgical facilities of different technical capacity. With nitrogen-bearing alloys, it is possible to produce the entire range of steels with any content of nitrogen. Master alloys are ecologically safe. Therefore, at present, nitrogen doping with master alloys remains the principal technological method for nitriding steel. Chromium, manganese, silicon, vanadium, etc. alloys can also be nitrided. The known 'furnace' methods for producing nitrogen-bearing alloys are characterized by long duration, high energy consumption and complexity of equipment. At that, they fail to provide a nitrogen-containing material that would combine high nitrogen content, high density and the minimum concentration of injurious impurities.

The self-propagating high-temperature synthesis (SHS), discovered by Merzhanov and his colleagues in 1967, appears rather promising for obtaining nitrided ferroalloys and master alloys. SHS was proposed as a method for producing high-melting inorganic compounds in an inert or reactive atmosphere [1]. To capture the advantages of SHS technology (such as the absence of power costs, extreme synthesis conditions of temperature and pressure, the possibility of obtaining materials with new properties, and others), we developed a new approach to the SHS process that is known as *metallurgical SHS process* [2]. This method uses various iron alloys as charge materials and allows disposing of dispersed waste and other substandard scraps.

The production of ferroalloys and other doping and deoxidizing materials for steel-making generates a vast amount of solid waste, mostly in powdered form. A significant part of such waste consists of dispersed materials that contain the main products, such as dopants, deoxidizing agents, and sometimes pure metals [3]. The powdered waste, including ferroalloys and other metal components, appears mostly when crushing raw materials and sorting them by fraction. At ferroalloy facilities, small fractions of materials accumulate when cropping and grinding ingots, and the plants cannot find use

for them. Ferroalloy fines can be added to the furnace during the main melting but, in practice, the larger part of powdered ferroalloy waste burns or gets lost with slag. In addition, powdered ferroalloys and deoxidizers get caught in the dust removal systems in the form of cyclone dust, which is formed during crushing, sizing and other operations with such ferroalloys as ferrosilicon, ferrochrome silicon, high-carbon ferrochrome, and others. Therefore, the problem of processing small fractions, which accumulate in large quantities in the production of iron-silicon ferroalloys, is still rather acute. For example, when grinding ferrosilicon of grades FS75 and FS65, there occur about 20 %wt. of 0–5 mm screenings and about 1% of micron-sized cyclone dust. The available methods of processing such waste have limitations for they can only recover small amounts of silicon at high power consumption. In particular, this applies to such methods as re-melting of lump material in induction furnaces, adding briquettes or extrusion products to the furnace during melting, adding the powder into molds, and blowing the powder into the furnace below the melting level [3].

The metallurgical SHS process is fundamentally different solution for disposal of cyclone dust and other ferroalloy wastes. The process can use various metallurgical alloys, including dust-like waste, as the main raw material. With minimal power consumption, the metallurgical SHS process allows obtaining high-quality nitrided ferroalloys and composite materials, based on iron-bonded inorganic compounds, for steelmaking and blast-furnace ironmaking.

The regular SHS process is induced by the heat of direct synthesis reactions [1]. In the metallurgical SHS process, ferroalloys act as the main reagents of the initial exothermic furnace charge, and the process occurs due to exothermic exchange reactions (Table 1). They are similar to metallothermic reactions [3].

TABLE 1: Exothermic reactions.

Regular SHS Reactions	Metallothermic Reactions	Metallurgical SHS Reactions
$Ti + B \rightarrow TiB_2$	$Fe_2O_3 + Al \rightarrow Fe + Al_2O_3$	$FeB + Ti \rightarrow TiB_2 + Fe$
$Zr + N_2 \rightarrow ZrN$	$B_2O_3 + Mg \rightarrow B + MgO$	$FeV + N_2 \rightarrow VN + Fe$
$Mo + S \rightarrow MoS_2$	$Cr_2O_3 + Ca \rightarrow Cr + CaO$	$FeTi + C \rightarrow TiC + Fe$
$Ni + Al \rightarrow NiAl$	$V_2O_5 + Al \rightarrow V + Al_2O_3$	$FeSi_2 + N_2 \rightarrow Si_3N_4 + Fe$
$Ta + C \rightarrow TaC$	$MoO_3 + Si \rightarrow Mo + SiO_2$	$FeB + N_2 \rightarrow BN + Fe$
$Ta + C + N_2 \rightarrow TaCN$	$MoO_3 + Si \rightarrow MoSi_2 + SiO_2$	$FeB + FeTi \rightarrow TiB_2 + Fe$
$Ti + Ni + C \rightarrow TiC + NiTi$	$B_2O_3 + TiO_2 + Mg \rightarrow TiB_2 + MgO$	$FeSi_2 + FeTi \rightarrow Ti_5Si_3 + Fe$
$Zr + Nb + C + N_2 \rightarrow ZrNbCN$	$Cr_2O_3 + Al + C \rightarrow Cr_3C_2 + Al_2O_3$	$NiB + Ti \rightarrow TiB_2 + NiTi$
$SiC + Ti \rightarrow Ti_5Si_3 + TiC$	$V_2O_5 + Al + N_2 \rightarrow VN + V_2N + Al_2O_3$	$FeTi + B_4C \rightarrow TiB_2 + TiC + Fe$
		$NiB + Ti \rightarrow TiB_2 + Ni$
		$CrN + Ti \rightarrow TiN + Cr$
		$CaC_2 + Ti \rightarrow TiC + Ca$

The main raw material for the metallurgical SHS process are ferroalloys, such as sili-cide (FeSi, $FeSi_2$, $MnSi_2$), intermetallides (VFe, TiFe), borides (FeB, FeB_n), solid solu-tions Cr(Fe) and their various combinations. The metallurgical SHS process, involving these inorganic compounds, generates a composite material based on nitrides, borides, silicide, etc. bonded with iron and/or an iron alloy. In terms of aggregate state of the initial reagents, the metallurgical (as well as regular) SHS process can be gas-free, gas-absorbing, and gas-yielding (Table 2). Figure 1 shows the differences in the combustion modes for these states.

TABLE 2: Examples of SHS modes.

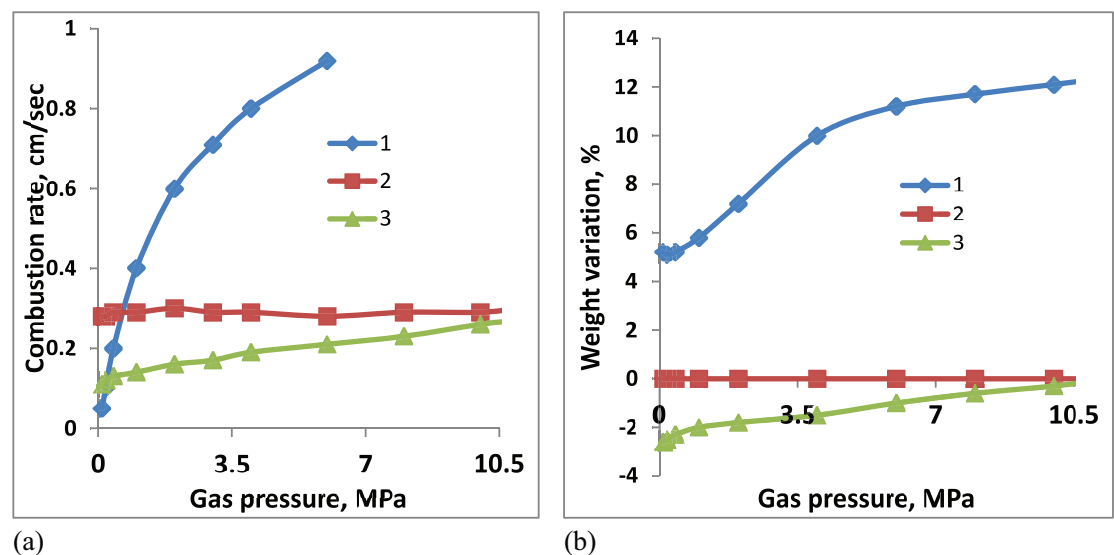|	Regular SHS Synthesis from elements	Metallurgical SHS Synthesis from alloys
Gas-free synthesis	Hf + C → HfC	FeB + Ti →TiB_2 + Fe
Gas-absorbing synthesis	B + N_2 → BN	FeTi + N_2 → TiN + Fe
Gas-yielding synthesis	Mo + S → MoS_2	CrN + Ti → TiN + Cr

(a)　　　　　　　　　　　　　　(b)

Figure 1: Influence of pressure on (a) combustion rate and (b) weight of samples:1 – (Fe-B) + Ti(Ar); 2 – (Fe-Ti) + N2; 3 – CrN + Ti(Ar).

1. SH-Synthesis Of Ferrosilicon Nitride

In the 1970s, a new refractory material ferrosilicon nitride (Si_3N_4-Fe) came into use in metallurgy. It was produced from Fe-Si powder, nitrided in a high-temperature resistance furnace. The main component of the alloy was silicon nitride Si_3N_4, the concentration of which reached 70–80%. Before that, silicon nitride had only been used as a ceramic material. The new material was developed for non-shape refractory mixtures as a hard-ening additive. Later, Si_3N_4-Fe was adopted by for steelmaking. Its main advantage was

a high nitrogen content (25–30 % N), which significantly reduced the consumption of alloying material.

During the synthesis of nitrides, the actual process temperature is lower than the calculated temperature due to the incomplete transformation in combustion. This is a result of melting of the furnace charge components and loss of permeability, or the low temperature of nitride dissociation. Both phenomena occur in response to nitriding of silicon. The adiabatic temperature of Fe-Si combustion in nitrogen is lower than the temperature of Si combustion due to the presence of Fe. The reason for the lower heat generation is the fact that Fe and Si are bound to thermally stable silicide. The adiabatic temperature of combustion is high for the alloys with different Si content (Table 3). Consequently, there is a favorable environment for SHS in the (Fe-Si) - N_2 system.

TABLE 3: Adiabatic temperature of ferrosilicon combustion in nitrogen.

Si content in ferrosilicon, %	Si_3N_4 content in combustion product, %	T_{ad}, ˚C
26.0	37.2	1535
45.0	57.7	3080
65.0	75.6	3790
70.6	80	3900
75.0	83.3	3930
90.0	93.7	4000

Ferrosilicon dust FS90 (89.9 % Si), FS75 (79.4 % Si), FS65 (68.1 % Si), and FS45 (48.25 % Si) was used for nitriding. The cyclone dust is a dusty fraction of ferrosilicon powder, which is formed during crushing and grading and accumulated in the dust removal system [4]. The pattern of Fe-Si combustion in nitrogen happened to be similar to the combustion of metallic silicon. The melting point of alloys in the Fe-Si system was lower than the melting point of Si. In alloys with Si content from 40 to 80%, the liquid phase appeared already at temperatures above 1,210 ℃. Hence the processes, associated with melting of the initial material during Fe-Si combustion, were more pronounced.

Figure 2 shows the influence of Si content in ferrosilicon on the combustion rate, the nitriding degree of the alloy, and the maximum temperature in the reaction wave. The data were obtained in laboratory conditions using, dust samples with particle size of 0.08 mm and less. As the Si content in the initial silicon alloy increases, the intensity of its interaction with nitrogen rises, which manifests itself in higher rate and higher temperature of combustion. The concentration of nitrogen in the combustion products also increases.
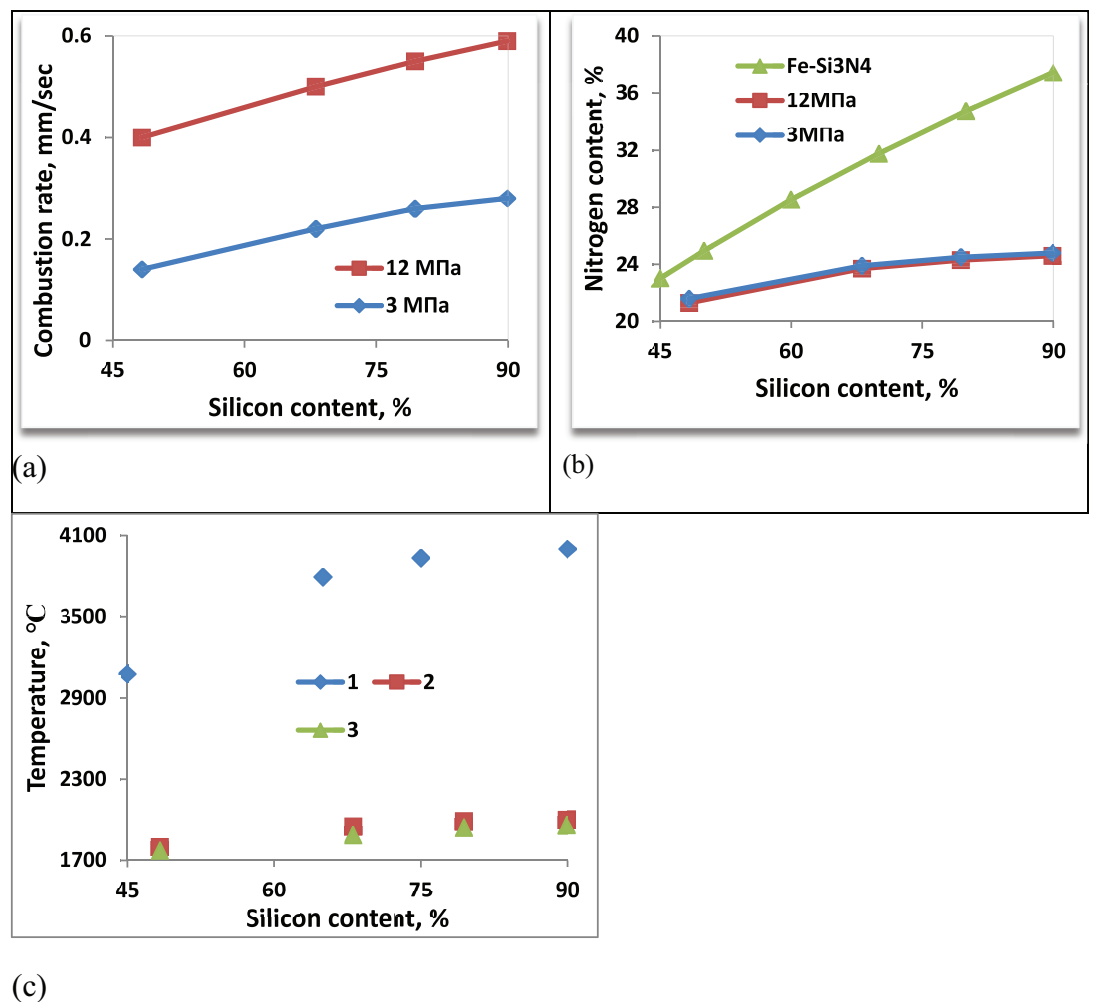
Figure 2: Influence of Si content in ferrosilicon on (a) combustion rate, (b) nitrogen content, and (c) combustion temperature: 1 – calculated, 2 – 12 MPa, 3 – 3 MPa. МПа – MPa.

The examination of the microstructure of burnt samples confirmed that molten ferrosilicon particles coagulate in the combustion wave. As a result, the reaction surface decreases, leading to incomplete conversion of silicon to nitride. The high temperature in the combustion wave enhances active melting of the initial particles. The X-ray phase analysis of the products of ferrosilicon combustion in nitrogen showed that β-Si_3N_4 remains the main phase in the entire range of initial parameters. Only insignificant amounts of α-Si_3N_4 were detected.

However, the furnace synthesis demonstrated a combination these two phases [5]. This can be explained by the fact that α-Si_3N_4 remains stable only up to ~ 1,400 ℃, and at a higher temperature it irreversibly transforms into the β-phase. The temperature of ferrosilicon combustion in nitrogen is over 1,750 ℃; therefore, the formation of α-Si_3N_4 becomes unlikely. The phase composition of the ferrosilicon nitriding products appears to be most influenced by the degree of Si → Si_3N_4 conversion. At the maximum

degree of conversion, the product is two-phase: β-Si_3N_4 + Fe. Unreacted silicon occurs as iron silicide. At that, the volume fraction of nitride exceeds 90%. This is due to the high concentration of silicon in the initial ferrosilicon and a large difference in the densities of Si_3N_4 and Fe. The energy-dispersive analysis by a scanning electron microscope showed that iron is distributed in the matter in the form of separate 'islets' islands ~ 200 µm or less in size. Such metallic inclusions are formed due to the fusion of molten iron and iron silicide, which are yielded during the nitride formation in combustion. The iron-containing inclusions are evenly distributed in the volume of combustion products. Figure 3 shows the microstructure of ferrosilicon nitride, and Table 4 presents the results of microanalysis.
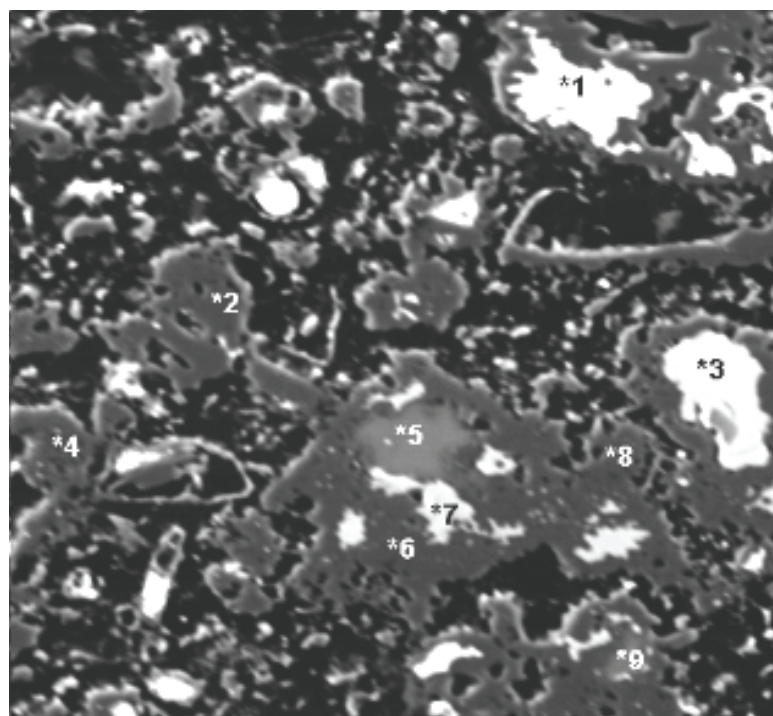
Figure 3: SHS microanalysis and microstructure of ferrosilicon nitride.

TABLE 4: Results of microanalysis ferrosilicon nitride; refer to Figure 3.

	1	2	3	4	5	6	7	8	9
Si	27.9	49.1	23.2	52.4	87.5	50.3	46.4	50.9	82.1
Fe	65.7	0.3	70.7	0.4	0.3	0.2	44.5	0.4	0.2
N	6.4	50.6	6.1	47.2	12.1	49.5	9.1	48.6	17.6
Phases	Fe-Si, Si_3N_4	Si_3N_4	Fe-Si, Si_3N_4	Si_3N_4	Si, Si_3N_4	Si_3N_4	Fe-Si, Si_3N_4	Si_3N_4	Si, Si_3N_4

Thus, the metallurgical SHS method allows synthesizing thermostable β-Si_3N_4-based materials using ferrosilicon as a raw material. The β-phase of nitride is quite efficient in non-shape refractory mixtures and can serves as a component of doping media. In

practice, it is optimal to use FS75 and FS90 alloys for manufacturing refractory materials, and high-purity alloys FS65 and FS75, for doping steel.

2. SH-Synthesis Of Nitrided Ferrovanadium

Industrial alloys (FeV80 (78.8 % V), FeV60 (59.2 % V), FeV50 (52.4% V), and FeV40 (41.6 % V) according to GOST 27130-94) and model alloys were used for nitriding of ferrovanadium in combustion. The former ones were obtained from industrial screenings (sub-standard fines of 5 mm or less), and the latter ones were made in a vacuum furnace by alloying powdered electrolytic vanadium (VEL-1, purity 99.8% V, Technical Specification TU 48-05-33-71) and high-purity carbonyl iron (OSCh 13-2, purity 99.98% Fe, Technical Specification TU 6-09-05808009-262-92). The alloys were melted twice to homogenize their composition. Alloys with calculated vanadium content of 80.0, 70.0, 60.0, 55.0, 48.0, 40.0, and 35.0 % V were obtained. The X-ray phase data showed that they were single-phase. The alloys with 60.0–80.0% V were α-V based solid solutions. The alloys with 35.0–55.0% V were σ-intermetallides.

The combustion rates of industrial and modelled alloys were similar (Figure 5a). Ferrovanadium can be nitrided in combustion if the V content is ∼ 40% or more. Similar to V and Fe powder mixtures, the combustion rate of the alloys decreases significantly as the V content falls from 80 to 60 %. When passing from ∼ 60% V to ∼ 55% V, the combustion rate increases sharply and then decreases again. At that, the nitrogen content in the combustion products decreases (Figure 5b).

When nitriding ferrovanadium, the combustion temperature (T_c) was measured with W-Re thermocouples BP5/BP20. Depending on the process conditions, maximum T_c varied from 1,780 to 2,060 ℃ for FeV80; from 1,630 to 1,830 ℃ for FeV60; from 1,480 to 1,560 ℃ for FeV50; and from 1,420 to 1,490 ℃ for FeV40. Thus, the more nitrogen is absorbed by the alloy, the higher combustion temperature is observed.

The layer-by-layer metallographic examination and the X-ray phase analysis of the samples, quenched to stop combustion, showed that nitriding of σ-Fe-V is activated due to the transformation of the intermetallide into a solid solution upon reaching the phase transition temperature (∼ 1200 ℃). Such activation causes the increase in the combustion rate for alloys with 35–55% V (Figure 4).

Ванадий лигатура – Vanadium master alloy

Ванадий ВЭЛ - Vanadium VEL

Промышленные сплавы – Industrial alloys

(a)

(b)
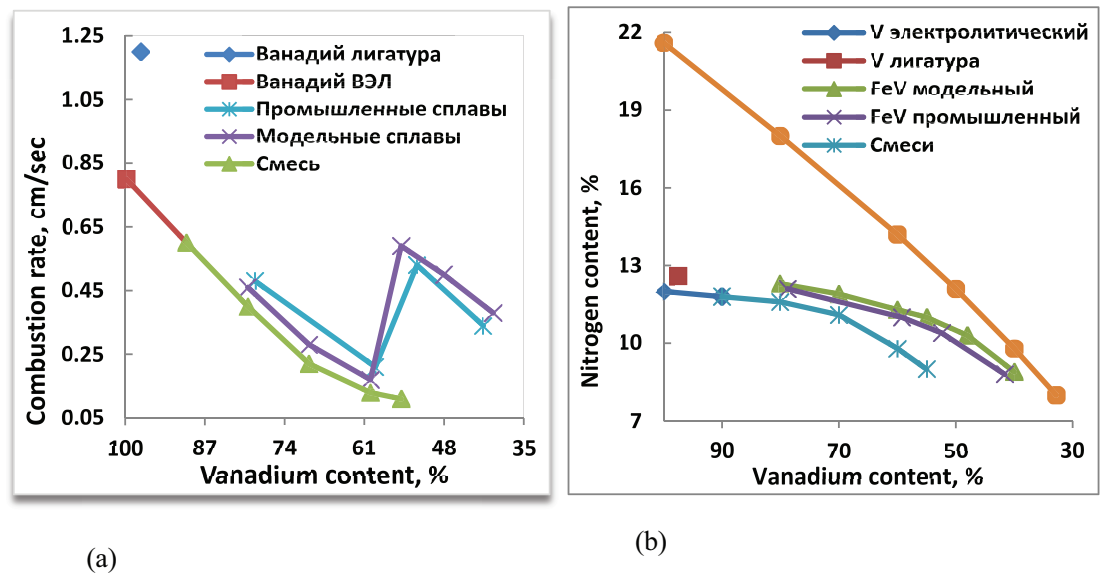
Figure 4: Influence of vanadium content on (a) ferrovanadium combustion rate and (b) nitrogen content in ferrovanadium.

Модельные справы – Modelled alloys

Смесь - Mixture

V электролитический – V electrolytic

V лигатура – V master alloy

FeV модельный – Modelled FeV

FeV промышленный - Industrial FeV

Смеси - Mixtures

The layer-by-layer X-ray phase analysis of the combustion zone of quenched samples confirmed the same. The initial powder was in the intermetallic σ-phase. In the area immediately adjacent to the combustion front, we detected a layer of particles, which was radiographically manifested as an α-solid solution. Along with the solid solution, the deeper layers contained δ-VN and α-Fe, the number of which increased rapidly. The final product was two-phase (δ-VN + α-Fe). The particles are heated by to the heat released in the nitride formation, and, upon reaching the melting temperature of the V-Fe-N eutectic, the liquid phase occurs. Further, a solid-liquid particle-droplet is formed, consisting of molten iron and solid vanadium nitride. Such semi-liquid particles combine into a solid-liquid layer, which is parallel to the combustion front. At the next moment, solid-liquid layer shrinks under the surface tension forces. Having fused, the mass crystallizes to form a dense material with a composite microstructure.

Two types of SHS-obtained ferrovanadium nitride FERVANIT were developed for industrial application: melted and sintered. The first one, in lumps, is intended for alloying

**Figure** 5: Industrial samples of melted ferrovanadium ni-tride FERVANIT.

of steel in a ladle or in a furnace (Figure 5). The second one should be used as a filler for cored wire to modify nitrogen content before casting. Table 5 gives the specifications of FERVANIT; the specification of Nitronvan Vanadium alloy is given for comparison. Melted ferrovanadium nitride has been tested in smelting of high-strength low-alloy steels, as well as rail and high-speed steel. Nitrogen recovery amounted to 86–98%; vanadium recovery, more than 95%.

TABLE 5: Composition and properties of nitrogen-bearing vanadium alloys.

| Properties	Vanadium alloy NITROVAN	SHS-obtained ferrovanadium nitride FERVANIT	
		melted	sintered
Raw material	$V_2O_5,$ V_2O_3, C	FeV40, FeV50	FeV60, FeV80
Chemical composition, %: V N C 0 S	76 – 81 10 – 18 1 – 10 < 1.5 < 0,5	44 – 48 9 – 11 < 0.5 < 0.5 < 0.1	55– 75 13 – 17 < 0.5 < 0.5 < 0.05
N:V (by weight)	1:5–1:6.5	1:4.5–1:5.5	1:4.5–1:6.5
Phase composition	VCN	VN. α-Fe(Mn)	V_2N. VN. α-Fe
Density, g/cm^3	2.5 – 3.0	6.0 – 6.5	4.5 – 5.5
Porosity, %	~50	<5	~40
Lump size, mm	33×28×23	10 – 60	< 100. < 2.5
Dust content, %	up to 5	none	up to 5
Strength, MPa	< 10	> 100	< 10
Nitrogen recovery, %	> 60	> 85	> 85
Vanadium recovery, %	> 75	> 95	> 90

3. SH-Synthesis Of Nitrided Ferrochrome

Nitrided Fe-Cr alloy is used in smelting of stainless and other grades of chromium steel, and nitrided Cr is used in production of Cr-Ni superalloys. Aluminum thermal treated Fe-Cr powder of grade PFN was chosen for experimental nitriding. This kind of ferrochrome (75.6 % Cr) melts at 1550–1670 ℃. In the range of nitrogen pressures from 2.0 to 10.0 MPa, the combustion temperature was 1220–1300 ℃ at $T_{ad} \approx 1680$ ℃. Therefore, nitriding took place by the solid-phase mechanism. The finer the ferrochrome powder, the more rapidly it is nitrided and the greater amount of nitrogen is recovered.
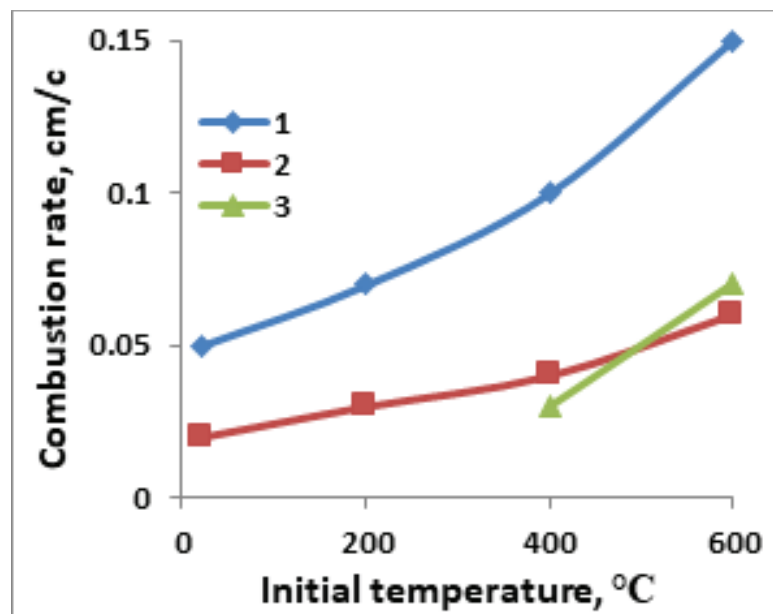
Figure 6: Influence of T_{ic} on ferrochrome combustion rate: 1 and 2 – 0.04 mm, 3 – 0.2 mm; 1 and 3 – 6 MPa, 2 – 2 MPa.

Larger fraction of alloy powder can be nitrided in combustion using either of two techniques: first, increase the temperature of the initial charge (Figure 6); second, use forced injection of the co-current inert and/or reacting gas into the combustion zone.

Combustion in the presence of forced gas filtration has been previously studied by the example of chromium nitriding [6]. In the co-current nitrogen flow ferrochrome burns at a high gas flow rate (Figure 7). The combustion rate of both Fe-Cr and Cr increases as the nitrogen consumption rises. At that, the nitriding degree of ferrochromium (4.7–7.5 % N) is less than its nitriding degree under the conditions of natural filtration (8.8–14.2 % N). The can be explained by the absence of a post-reaction 'maturing' stage in case of forced nitrogen filtration. Quenching nitrided products with incoming gas flow fixes the amount of nitrogen that was absorbed directly in the combustion zone.

(a) (b)
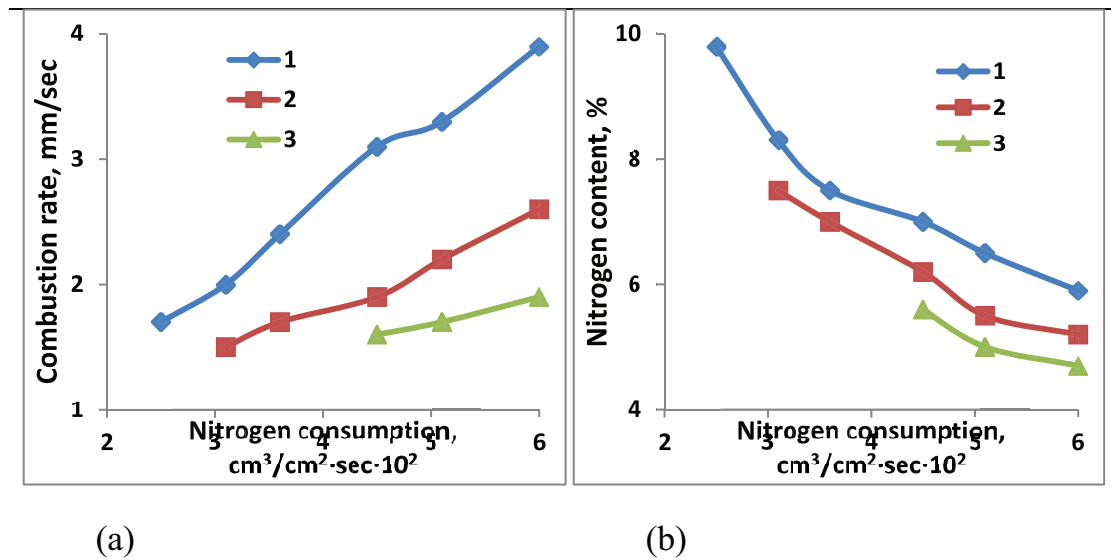
Figure 7: Influence of N_2 specific consumption on (a) combustion rate and (b) nitriding degree: 1 – Cr, 2 and 3 – Fe-Cr; 1 and 2 – dispersion of 63–80 µm, 3 – 63–200 µm.

The metallographic analysis of combustion products did not reveal any traces of melting. The solid-phase mechanism facilitates a high nitriding degree of Fe-Cr. However, the maximum degree of nitriding could not be attained in the nitriding of ferrochrome. The limiting nitrogen concentration is ~ 16.8 % N for alloys with 75.6 % Cr, while the actual nitrogen content in the ferrochrome was ~13.0 % N. Thus, the maximum nitriding degree is ~ 77 % of the calculated value. The main phases in the ferrochrome combustion products and the furnace alloy were CrN, Cr_2N, $(CrFe)_2N$, and Fe. Four grades of Cr-based master alloys were developed for industrial application in steelmaking (Table 6).

TABLE 6: Industrial grades of SHS-nitrided ferrochrome/chromium.

Alloy Properties		Nitrided ferrochrome		Nitrided chromium	
		Melted	**Sintered**	**Melted**	**Sintered**
Chemical composition, %	N,%	6–8	8–13	8–12	16–20
	Cr,%	62–76	60–72	88–91	79–82
	C,%	0.05 0.10	0.03 0.10	0.03 0.06	0.03 0.06
	O,%	0.3	0.3	0.2	0.2
Phase composition		$(Fe,Cr)_2N$, Fe	$(Fe,Cr)_2N$, CrN, Fe	Cr_2N	CrN, Cr_2N
Density, g/cm^3		6.0–7.0	4.3–5.3	5.5–6.6	3.4–4.6

The reduced nitrogen content in fused nitrided ferrochrome/chromium, in contrast to sintered alloys, can be explained by the fact that nitrogen occurs in the material in the form of lower nitride Cr_2N as a result of partial dissociation of chromium mononitride CrN.

The microstructure and the microanalysis of nitrided ferrochrome are shown in Figures 7 and 8. The microanalysis results are interpreted in Table 7.
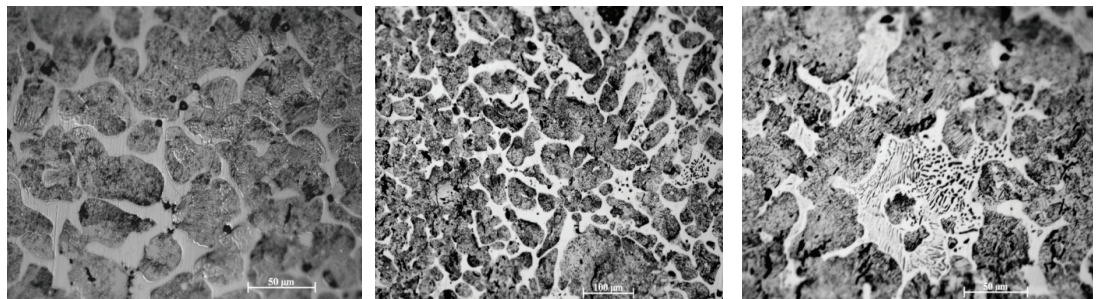
Figure 8: Microstructure of melted nitrided ferrochrome. The darker areas are nitrides Cr_2N and $(Cr,Fe)_2N$; the lighter areas are iron with dissolved chromium and nitrogen.

x500   Cr   Fe
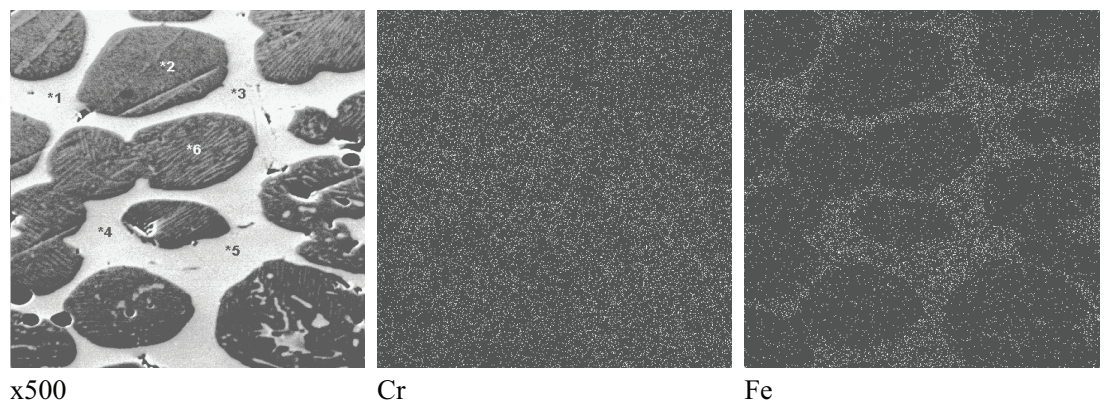
Figure 9: Microanalysis of melted nitrided ferrochrome.

TABLE 7: Microanalysis fused nitrided ferrochrome; refer to Figure 8.

	1	2	3	4	5	6
Cr	57.73	82.80	66.56	66.15	57.63	78.13
Si	5.66	0.23	4.30	4.28	5.74	1.39
Fe	33.15	6.28	25.27	27.55	33.53	13.29
N	3.44	10.67	3.85	2.00	3.09	7.17

Figure 9 shows a batch of sintered nitrided ferrochrome FHN10.

New nitrogen-bearing master alloys of Cr, V, Si, Mn, etc. has already found use in steelmaking in Russia and abroad. Steel grades 12H18AG18, 35H2AF, 55H21G9AN4, 16G2AF, 110G13HPAL and nickel-chromium alloy with ~ 0.5 % N were produced with the proposed method.

The laboratory studies helped to create the industrial SHS technology for production of nitrided ferroalloys, master alloys, and other materials based on oxygen-free compounds (Table 7). The technological process includes the following stages: preparation of the exothermic charge, synthesis of composite alloys by combustion, and processing of synthesis products. Synthesis by combustion is carried out in industrial vertical-type reactors with reaction space of 0.15 m^3. NTPF Etalon Ltd (Magnitogorsk, Russia) produces SHS materials for metallurgy. Etalon's facilities include crushing and grinding units, crucible dryers, SH-synthesis equipment, control rooms, quality control laboratories, chemical laboratories, and warehouses of raw materials and finished products. The SH-synthesis shop operates 40 SHS reactors and can produce up to 10 tons of nitrided products per day. The SHS technology in metallurgy has completely supplanted the vacuum-thermal technology of the nitrided master alloy production. The production plan of the new shop focuses on specialized compositions of refractory materials and doping materials for steelmaking (Table 8).

Figure 10: Industrial samples of sintered nitrided ferrochrome FHN10.

In conclusion, a scientifically grounded industrial SHS technology was created for producing nitrided ferroalloys and composite materials based on oxygen-free compounds in steelmaking and blast-furnace ironmaking. The principal problem of creating a large-scale SHS-based production facility has been solved. A new approach to the practical implementation of SHS method was developed. The possibility of using synthesis

TABLE 8: Etalon's SHS materials for steelmaking.

SHS material	Customers	Application	Production volume in 2008-2017
Nitrided ferrovanadium / ferrovanadium nitrideFERVANIT®	EVRAZ Consolidated West-Siberian Metallurgical Plant, EVRAZ Nizhny Tagil Metallurgical Plant, Chelyabinsk Metallurgical Plant, Azovstal Iron and Steel Works	Rail and structural steel~ 500 thousand tons	Mass production ~300 tons
Nitrided low carbon ferrochrome / ferrochrome nitride CHROMANIT	JSC Izhstal, JSC Electrostal, Magnitogorsk Iron and Steel Works, F.W.Winter Inc & Co	Stainless steel, electrodes ~ 20 thousand tons	Mass production ~200 tons
Nitrided chromium / chromium nitride CHROMANIT	NPO Saturn	Stainless steel, electrodes	Mass production ~300 tons
Nitrided Ferrosilicon-NITROFESIL®A	Magnitogorsk Iron and Steel Works, NLMK Group	Transformer steel, 200 thousand tons per year	Mass production ~300 tons
Silicon nitride-based hardening additives NITROFESIL®AL, NITROFESIL®TL, REFRASIN	Magnitogorsk Iron and Steel Works, TRB refractories	Tap hole clay and runner clay, 80 thousand tons per year	Mass production ~2500 tons
Nitrided manganese, ferromanganese and silicomanganese	Chelyabinsk Metallurgical Plant, Oskol Metallurgical Plant	Rail and structural steel	Mass production
Antioxidants BorTiX® Borides (AlB_2-AlB_{12}, TiB_2) Nitrides (AlN, Si_3N_4)	Magnezit Group, LLC Ogneupor	Carbon refractories	Pilot batches
Ferrotitanium silicon Ferrotitanium boride	Magnitogorsk Iron and Steel Works, Zlatoust Metallurgical Plant	Structural and pipe steel	Pilot batches

products in metallurgy was demonstrated by involving ferroalloys in the research. The metallurgical SHS process, based on various alloys as raw materials, including dusty wastes of the ferroalloys production, extends the boundaries of synthesis by combustion. The problem of micro-alloying of steel with nitrogen, boron and titanium in smelting of high-quality steels was solved by creating a new class of master alloys—composite alloys based on nitrides, borides and silicide of titanium, vanadium, chromium, and other transition metals. Specialized SHS reactors with reaction space of 0.06, 0.15, and 0.3 m^3 were designed for mass production of refractory inorganic compounds. Scientific and technical production company Etalon established the industrial-scale SHS production

of composite materials based on oxygen-free compounds in Magnitogorsk, Russia. The capacity of new production facility is 5 thousand tons of SHS products per year.

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