## Microalloying of Steel with Vanadium and Nitrogen

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Received July 2, 2014

**Abstract**—The microalloying of steel with vanadium and nitrogen is experimentally studied. The goal is to compare the results when steel is alloyed with standard ferrovanadium and vanadium converter slag (with gaseous nitrogen injection) and with nitrided ferrovanadium. These methods of microalloying are equivalent in terms of the attainment of the required vanadium concentrations. All the steel samples have a fine-grain structure, which means that the method of vanadium introduction has little influence on the final structure.

*Keywords*: microalloying, vanadium, gaseous nitrogen, reduction with carbon **DOI:** 10.3103/S096709121410012X

Vanadium is in great demand as a microalloying element, since it imparts very valuable properties to steel.

Like most modifying elements, vanadium affects the properties of steel by reducing the grain size and by dispersional hardening and, to a lesser extent, by strengthening the solid solution. With reduction in the grain size, the strength and ductility of the steel improve. Fine deposits increase the strength at the expense of some ductility. However, reducing the grain size improves the welding properties of the steel. The formation of vanadium carbonitrides with good solubility in steel eliminates the negative effect of nitrogen, which then plays a significant role in amplifying the dispersional hardening in the presence of vanadium. In addition, the size of the recrystallized austenite grains in steel alloyed with vanadium is constant over a broad temperature range. Therefore, the properties of such steel do not depend on the rolling temperature. In comparison with niobium and titanium, vanadium has the following benefits as an alloying element [1]:

-greater solubility of vanadium carbonitrides in austenite;

—the ability to obtain small austenite grains without slowing recrystallization, since vanadium phases are deposited below the final rolling temperature;

—the potential for less expensive high-temperature controlled rolling;

—considerable reduction in the hot cracking of the alloyed steel when bending and straightening continu-ous-cast billet;

—good strength and ductility of the alloyed steel in the thermal influence zone with correct choice of the welding parameters, even with a high nitrogen content. The reduction in grain size and dispersional hardening produced by vanadium are more pronounced in the presence of nitrogen, which is converted from a harmful impurity to an alloying element. That is especially important for steel produced in arc furnaces.

In alloying steel, vanadium is generally introduced by means of ferrovanadium, as well as alloys obtained directly from vanadium slag. Other possible sources are vanadium hot metal, vanadium slag of standard and special composition, vanadium-bearing products obtained on crushing vanadium slag, reduced pellets, and exothermal briquets. As a rule, these sources are used in the production of low-alloy steel [2, 3].

Nitrogen is usually introduced in steel by means of materials with a high content of dissolved nitrogen and also nitrogen compounds that readily decompose at metallurgical temperature, with the activation of molecular nitrogen and its solution in the liquid metal.

A deficiency of such methods is the need to produce special ferroalloys of compounds; the unstable assimilation of nitrogen from those compounds on alloying; and the nonuniformity of the nitrogen content in the final steel.

Obviously, alloying with gaseous nitrogen is environmentally and environmentally preferable. However, the energy required to activate the intermolecular bonds in gaseous nitrogen is an obstacle. Active research on the alloying of steel by means of gaseous nitrogen has been underway for some time now, in Russia and elsewhere [4].

To determine the injection conditions for gaseous nitrogen and assess its assimilation, we analyze data from the electrosmelting shop at OAO EVRAZ ZSMK regarding the smelting of CT3CI, 09 $\Gamma$ 2C, and H $\ni$ 76 $\Phi$  steel with the injection of gaseous nitrogen through bottom lances in the ladle treatment system.



Fig. 1. Dependence of the quantity of assimilated nitrogen on the injection time.

In Fig. 1, we plot the assimilation of nitrogen against the injection time. In Fig. 2, we present the increment in the steel's nitrogen content as a function of the total quantity of gaseous nitrogen introduced.

We see that the assimilation of nitrogen increases from 20 to 37% when the injection time increases from 30 to 60 min. With increase in the consumption of gaseous nitrogen, its content in the steel increases: from 0.002% with 10 m<sup>3</sup> consumption of gaseous nitrogen to 0.005% with 20-22 m<sup>3</sup> consumption.

The high correlation coefficient obtained in the statistical analysis of Fig. 2 indicates stable assimilation of nitrogen by the melt. That permits fairly precise regulation of its final content in the steel during microalloying.

In laboratory conditions, we conduct a series of experiments on the microalloying of steel with vanadium and nitrogen. The goal is to compare the results



Fig. 2. Increment in the steel's nitrogen content as a function of the total quantity of gaseous nitrogen introduced.

when steel is alloyed with standard ferrovanadium and vanadium converter slag (with gaseous nitrogen injection) and with nitrided ferrovanadium. The composition of the ferrovanadium is as follows:

	Content, %								
Grade	V	Si	Al	С	S	Р	Ν		
FeV40	37.8	1.8	2.1	0.3	0.08	0.07	_		
VD1	38.1	1.7	1.6	0.3	0.07	0.07	4.38		

The composition of the vanadium slag is as follows:  $16.0\% V_2O_5$ ,  $20\% SiO_2$ ,  $5\% TiO_2$ , 10% MnO, and 30% FeO.

Table 1 presents the composition of the initial samples produced for the experiments. In the experiments, a crucible with the selected batch is placed in a resistance furnace with a pipe heater. The furnace is

Content, wt % Sample С Si Mn Cr Ni Cu V Ν 1 0.23 0.50 0.50 0.05 0.09 0.12 0.001 0.006 2 0.16 0.54 0.54 0.05 0.08 0.11 0.001 0.005 3 0.22 0.46 0.51 0.06 0.09 0.12 0.001 0.006 4 0.06 0.10 0.001 0.20 0.48 0.480.14 0.007 5 0.19 0.43 0.41 0.05 0.08 0.13 0.001 0.005 6 0.21 0.51 0.58 0.06 0.12 0.08 0 0.004 7 0.09 0.001 0.24 0.38 0.54 0.05 0.12 0.006 8 0.22 0.31 0.48 0.06 0.08 0.13 0.001 0.004 9 0.0003 0.19 0.60 0.41 0.05 0.09 0.12 0.005 10 0.24 0.39 0.50 0.04 0.05 0.09 0.001 0.006

 Table 1. Composition of initial samples

Series	Initial sample	Content, wt %								
		С	Si	Mn	Cr	Ni	Cu	V	Ν	
1	4	0.19	0.37	0.45	0.05	0.10	0.14	0.13	0.012	
	7	0.23	0.27	0.48	0.05	0.09	0.12	0.12	0.011	
	10	0.23	0.27	0.45	0.04	0.05	0.09	0.13	0.010	
2	5	0.19	0.44	0.39	0.06	0.08	0.13	0.13	0.010	
	6	0.20	0.50	0.55	0.05	0.12	0.08	0.13	0.009	
	9	0.19	0.59	0.39	0.04	0.05	0.09	0.12	0.011	
3 nitrided ferrovana- dium	1	0.22	0.37	0.39	0.06	0.09	0.12	0.12	0.010	
	2	0.24	0.39	0.41	0.05	0.08	0.11	0.13	0.009	
	3	0.20	0.30	0.34	0.06	0.09	0.12	0.13	0.011	

 Table 2. Composition of steel produced

sealed by a graphite stopper with holes containing two tubes of high-alumina refractory: nitrogen is supplied to the furnace through one tube, so as to create a gaseous atmosphere, and leaves the furnace through the other. The temperature is recorded by means of a VR 5/20 tungsten—rhenium thermocouple.

Three series of experiments are conducted. In the first, the steel is alloyed with standard FeV40 ferrovanadium, with nitrogen injection.

The initial steel sample is melted at 1823 K, and ferrovanadium is added. After isothermal holding for 5 min, nitrogen injection begins, continuing for 30 min. The results are shown in Table 2.

In the second series, after the steel sample has melted, the crucible is closed with a lid containing tubes through which nitrogen enters and leaves. Nitrogen injection lasts for 20 min, and then briquets made from vanadium converter slag, a mixture of reducing agents (coke fines and ferrosilicon), and lime are introduced at the steel surface. The briquet composition is selected by thermodynamic modeling of the reduction of vanadium from the vanadium pentoxide in vanadium converter slag by means of carbon [5, 6]. After 5-min isothermal holding at 1823 K, injection of nitrogen into the steel continues for 10 min. Table 2 presents the composition of the metal produced.

In the third series, the steel samples are microalloyed with VD1 nitrided ferrovanadium. The composition of the resulting metal is presented in Table 2.

The quantity of ferrovanadium employed is based on a target vanadium content of 0.15% in the final steel and 95% assimilation and also on 90% assimilation from converter slag, with nitrogen contents of 0.01 and 0.015% in the steel.

Analysis of the results shows that the nitrogen content in the final steel is 0.009-0.012%. The Increment in the steel's nitrogen content is 0.005%, on average, and does not depend on the nitriding method. The vanadium content in the final steel is 0.12-0.13% in all cases.

In Fig. 3, we show the microstructure of the steel samples obtained. We see that all the samples have a fine-grain structure.



Fig. 3. Microstructure of the steel samples obtained: (a) for standard ferrovanadium and gaseous nitrogen; (b) for vanadium converter slag and gaseous nitrogen; (c) for nitrided ferrovanadium.

STEEL IN TRANSLATION Vol. 44 No. 10 2014

## CONCLUSIONS

The results show that all the methods of microalloying are equivalent in terms of the attainment of the required vanadium and nitrogen concentrations in the metal.

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Translated by Bernard Gilbert