Development of Nitrogen Vanadium Alloyed Steels by Enhancing the Nitrogen Recovery

RBV Ramana[1], Kunthal pal
[1] Tata Steel Ltd, Jamshedpur works, India
E-mail: [1]ramana@tatasteel.com

Abstract

Tata steel, Jamshedpur produces 9.4 million tonne of steel comprising a wide basket of steel grades in the long and the flat product segment. The product basket comprises of micro alloyed steels for automobile and the construction applications. Higher strengths for these steels are achieved by alloying the steel with Niobium, Vanadium and Titanium.

An incremental strength of 100 to 200 Mpa is achieved by alloying the steel with .03 to .05% Vanadium and Nitrogen in the range of 80 to 120 ppm. Presence of vanadium and nitrogen in a stoichiometric ratio of 4.5 /1 to 5 / 1 promotes the formation of fine precipitates of vanadium nitride which results in the strengthening of the steel. Liquid steel produced at Tata steel contains nitrogen in the range of 40 to 50 ppm after tapping from the BOF. The nitrogen content of the steel needs to be enhanced during the subsequent ladle furnace process. Four distinct methods were investigated for enhancing the nitrogen recovery and to increase the nitrogen content of the steel. Predictable achievement of the required amount of nitrogen could be achieved by slag free tapping, proper deoxidation practices, method of addition of Nitro vanadium alloy and by ensuring higher recovery of nitrogen with the usage of bottom argon purging at the ladle furnace.

A reliable process was developed by optimising the deoxidation, addition and purging parameters. Further optimisation was achieved with the trials carried out by the development of nitro vanadium cored wire in collaboration with M/s Sarthak industries. An optimised V : N ratio of 4.75 to 5 was achieved with the usage of the cored wire of nitro vanadium. The desired mechanical properties of vanadium and nitrogen alloyed HSLA steels were fully achieved and the needs of the customers were fully met. Internal rejections due to inferior mechanical properties in these steel grades were reduced to zero.

Key words : Vanadium and Nitrogen Recovery, Cored wire injection

Introduction

Micro alloyed rebar grade production at LD1

- Requirement of nitrogen and vanadium in steel

  Air cooled microalloyed rebar is a new grade being developed by Tata steel. The steel is being used as earth quake resistant steel. The UTS/YS ratio of these steels should be > 1.25. To obtain the requisite strength through precipitation strengthening, the alloying of grade requires vanadium between 0.04 to 0.05 % and nitrogen content between 100 to 120 ppm. Vanadium forms carbides and nitrides which result in strengthening of the steel.

- Developmental work done at lab scale has shown that V and N in the ratio of 4.5 / 5.1 is gives the highest YS and UTS to the steel.

Methods for increasing Nitrogen in steel.

In steel grades with similar C and Mn contents, the nitrogen content in the billet samples vary from 70 to 80 ppm. An incremental content of 30 to 40 ppm is required for achieving the required chemistry of the steel.

Nitrogen content in the steel can be enhanced by the following methods:

- Blowing of liquid steel with nitrogen at the end of blowing at BOF
- Purging of the liquid steel after killing the bath and with 50% Desulphurization
- Addition of N bearing alloys like nitrided vanadium
- Addition of N bearing alloys like nitrided manganese - used at TSE

The first two options were evaluated. The 2^{nd} option involves change over from argon to nitrogen and back to argon during the processing of the heat at ladle furnace. However, due to the operational constraints at LD1, the first two options were not considered.

Nitrided vanadium was used on trial basis for micro alloying in a few heats at LD2. Analysis of data for a similar grade with a matching chemical composition has indicated that 30 to 40 ppm of nitrogen can be obtained with a standard operating practice for the addition of nitro vanadium. When using nitrovan products, either nitrovan 12 or nitrovan 16, it is convenient to have an approximate value for expected nitrogen recovery in the liquid steel. Experience at LD 2 and a few other steel plants has shown that for optimized industrial operation, it is expected that 10 ppm nitrogen will be added for each 0.01 % V added as nitrovan 16. Mass balance calculations demonstrate that the recovery of the nitrogen from the alloy addition is from 60 to 70 %. Vanadium recovery from nitrovan additions is > 90 % with good addition practices.

While a 60 % recovery seems to be a low value for alloy additions, it is actually quite high for additions of elements that naturally occur in gaseous form. The actual recovery obtained is dependent, to a great degree, on the solubility of the element in the steel and the alloy addition practices used.

When adding nitrovan products to liquid steel, the briquettes dissolve quite rapidly. Nitrovan contains 12 % to 16 % nitrogen. The maximum solubility of nitrogen in liquid carbon steel, on the other hand, may be as little as 0.03%. When the solubility of nitrogen in the liquid steel is exceeded, the nitrogen will come out of the steel, forming N_2 gas. Once that occurs, the nitrogen gas will rise to the top of the steel bath and escape into the atmosphere. This nitrogen bubbling out of the steel may appear as a “foaming” action in the slag cover of the steel. The loss of atomic nitrogen to nitrogen gas is the primary reason for reduced recovery rates of nitrogen.

Based on this limitation, the key to optimizing the recovery of nitrogen during nitrovan additions is to minimize the chances for nitrogen to exist in the steel at concentrations significantly above the solubility limit. Since the nitrovan nitrogen content is well above the solubility limit of nitrogen in steel, and the nitrovan is dissolving rapidly, it is most important that the steel is vigorously stirred during the time the nitrovan is dissolving. Vigorous stirring of the steel will reduce the time available to build up high levels of nitrogen in a localized area of the liquid steel. Also, slow additions of the nitrovan alloy can reduce the chances for localized concentrations of briquettes causing a high concentration of dissolved nitrogen.

Due to the reasons mentioned above, nitrovan additions into the ladle during tapping of the steel are a proven practice. This is practised in US based steel plants. The aggressive stirring action of the steel pouring into the ladle can be effective for improving nitrogen recovery. Nitrovan can also be added later in the ladle, but should be done when the stirring action is at a high level.

- Recovery rates of dissolving nitrogen will also be affected by the “window” of opportunity defined by difference between the bulk nitrogen level and the maximum solubility of nitrogen for given steel conditions. The higher the nitrogen aim point, the more care should be taken to maximize recovery. Addition of nitro vanadium can be done at the following stages.

At LD1, the following options were considered for the addition of nitrovan.

a) During the tapping of liquid steel

At LD1, there is no facility to purge the steel with argon during tapping. Mixing of the alloys takes place because of the turbulence generated during tapping. In addition, the BOF at LD1 is not equipped with a slag detection or slag stopping facility. Any slag carry over during tapping will result in low recovery of Vanadium.

b) Secondary steelmaking

Stirring of the liquid steel through the bottom porous plug is started after the ladle reaches one of the LF stations. Due to the above reasons a decision was taken to add NV16 after the following conditions are met:

- Bottom porous plug is functional
- Temperature of liquid steel > 1560^0C
- Fluid slag with no icebergs of lime
- Analysis of heat data at LD2
- With the usage of NV16 lumps, identification of the critical process variables for good nitrogen recovery is essential. Analysis of data with the usage of NV16 at LD2 reveals variability of nitrogen. Slag conditioning is the important variable there, as the V can only be lost to the slag. V is lost to the slag because of trapping of the NV in the crusty slag. This will result in low V recoveries as well as low N recovery. Presence of fluid slag with good aggressive stirring at the time of NV addition at the LF is critical. Nitrogen absorption requires good contact between the metal and the alloy, at least for five minutes immediately after the addition.
- Nitro vanadium lumps additions are done in all heats irrespective of initial S% level. It was observed that the vanadium and nitrogen recoveries were normal. The reason can be attributed to the vigorous stirring required for the slag-metal interaction. This is an enabler for maximizing nitrogen recovery. From

the analysis, it is recommended to add nitrovan immediately upon starting the vigorous stirring at the ladle furnace, regardless of the S level. Benchmarking of the operational practices of some of the steel plants was done. At the melt shop of Gallatin steel which produces HSLA, NV16 is added at the ladle furnace. Gallatin steel uses Nitro vanadium both as lumps and cored wires and aim V levels in these grades, typically from 0.12 to 0.15 % V with a nitrogen level of 190 ppm.

- Data showing recovery comparison (shown in annexure) of nitrogen and vanadium with the utilization of nitrovan 16 in bags and as cored wire was obtained from Gallatin steel which is equipped with a thin slab direct roll strip mill, with EAF and LAF refining. Bag additions are done at the LAF, as well as the wire feeding. The average recoveries were observed to increase from 55% to 70% and the standard deviation in heat to heat recovery is substantially reduced. The recovery rate does decrease as the final N content increases. This is to be expected as the maximum solubility of N in the liquid steel is 300 to 400 ppm. After approaching the threshold level, it becomes more difficult to add N. Unlike TSL, Gallatin steel based at the USA is a EAF based facility. Gallatin steel produces HSLA steels with nitrogen contents >150 ppm in some of the steel grades. The enablers at Gallatin are the following :

  - No carry over slag from the EAF. Vanadium recovery reported is > 95%.
  - Addition of NV16 during tapping with bottom argon purging in the ladle.
  - Development and usage of NV16 cored wire at the ladle furnace.

Trials and results

Trial number 1

Three heats were produced in the first trial. The heats were made with the addition of the lumps of nitro vanadium. The heats were produced through the LF3- CC3 route. The chemical composition of the steel grade is -

	C	**Mn**	**Si**	**P**	**S**	**V**	**N**
Min	0.20	1.5	0.40			0.04	90
Max	0.24	1.6	0.45	0.03	0.025	0.05	120
Aim	**0.22**	**1.55**	**0.42**	**0.020**	**0.020**	**0.045**	115

To reach the desired Si specification, Si-Mn and Fe-Si were used as the bulk alloy additions.

At the ladle furnace, NV16 lumps were added after the confirming the following parameters.

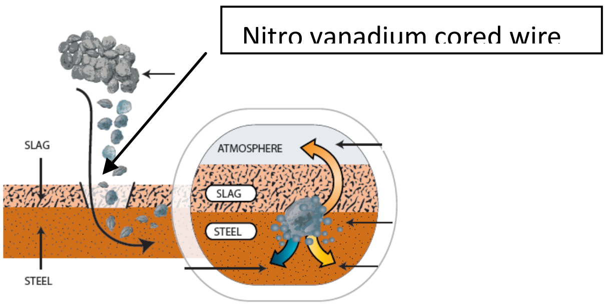
- Argon bottom purging with a purging eye > 200 mm
- Argon flow rate at a flow rate > 25m^3/hr
- Fluid slag
- Liquid steel temperature > 1570^{0}C
- No carry over slag from the vessel

The chemical composition of the three heats cast in the first trial is mentioned below. The V recovery varied between 95 to 96 %. Nitrogen recovery varied from 30 to 40%.

Cast No.		C	Mn	S	P	Si	Cr	V	N_2
		%	%	%	%	%	%	%	ppm
M89673	Tundish	0.22	1.52	0.011	0.02	0.45	0.028	0.051	105
	Billet	0.22	1.5	0.012	0.02	0.42	0.036	0.0497	100
M89675	Tundish	0.222	1.52	0.01	0.017	0.44	0.027	0.048	105
	Billet	0.22	1.51	0.011	0.02	0.42	0.022	0.0495	100
M89679	Tundish	0.23	1.54	0.009	0.02	0.44	0.031	0.047	94
	Billet	0.21	1.52	0.01	0.02	0.42	0.025	0.0462	96

Trial number -2

To enhance the Nitrogen recovery and obtain the V/N ratio of 4.5, nitro vanadium cored wire produced by Sarthak metals was used in the second trial. The nitro vanadium cored wire of 13 mm diameter with a sheath diameter of 1 mm was used for the trials. NV16 wire was used at one of the ladle furnaces for the production of the micro alloy rebar heats cast at CC3.



- The average recovery of vanadium from the NV wire is 98 %.
- The recovery of nitrogen from the NV cored wire varied from 60 to 70 %.
- The 13 mm wire was fed at a speed of 200 m/minute with the bottom argon purging rate of 15m^3/ hour
- All the heats were cast at caster 3. Data of a few heats is shown below.

Heat no	C	Mn	Si	P	S	Al	V	N
M98649	0.21	1.55	0.43	0.021	0.011	0.002	0.046	96
M98652	0.21	1.57	0.43	0.021	0.015	0.002	0.05	98
M98654	0.218	1.57	0.43	0.02	0.019	0.002	0.045	107

Table - NV16 - Comparison between lumps and Cored wire

Parameter	NV lumps	NV cored wire
Type of addition	Manual through LF slag door	Through wire feeder
Safety issues	Chances of injury to the operator during addition	Safe
Mix up with other micro alloys	Yes	No
Weighing of alloy before addition	Prone to error	Precise
V recovery	93 to 94%	97 to 98%
N recovery	30 to 40%	40 to 50%
Flexibility	Needs to be added at start of LF process	Can be added during any stage of the process

Conclusion

Injection of the cored wire deep into the ladle utilizes the higher ferrostatic head (pressure) at that point to maximize the nitrogen absorption into the steel. Also, deep penetration maximizes the dissolution time that the particles are surrounded by only steel, as nitrovan is less dense than steel and tends to rise to the steel/slag interface. Because of the fine particle size, the large surface area of the alloy available to the steel results in fast dissolution of the nitrovan alloy addition. Those are the reasons for the higher recovery rate of nitrogen when injecting nitrovan by wire feeding.

Another advantage of wire feeding is that it can be added to the steel late in the refining process, without the need for the aggressive stirring. In Tata steel the residual N level after tapping from the BOF is between 30 - 40 ppm.This makes the use of Nitro van useful for the micro alloying of rebars. It is expected that an additional 40 to 50 MPa yield strength will result just from the nitrogen addition at this vanadium level. The resulting ratio of V: N is around 4.5. For this case, the use of wire feed over bulk results in an additional 10 to 20 ppm N, which results in an additional 7 to 15 MPa YS on an average.

Based on the above, it is concluded that injection of nitrovan cored wire is the ideal input for reaching the targeted V and N in the micro alloyed rebar.

However the cost of NV16 when used as a cored wire is approximately 15 to 20 % higher than the cost of NV16 lumps. With process optimization it is possible to reduce the difference between the wire and lumps to about 10 %. Trials are being continued to establish the cost effectiveness with the usage of NV16 cored wire.