CBMM
Niobium Nb

Guidance on Making Ferroniobium Additions During Ladle Steelmaking

Optimizing Niobium Recovery

Over 90 percent of CBMM's production is supplied for use in the world's steel industry.

Niobium has an established niche in many types of steel products because of its unique ability to improve strength, toughness and weldability. About 15 percent of ferroniobium (FeNb) ends up in stainless steel production, which is an important growth sector, but the vast majority is currently consumed in the production of what we call high strength low alloy (HSLA) steels, often also referred to as microalloyed steels.

The successful production of all these steels requires careful control of the niobium level and, after casting, the niobium must be consistently present in a form, which during subsequent processing, will enable it to produce the desired metallurgical effects.

It is important that steelmakers can confidently predict their final compositions and they need to be able to rely on a reproducible 'yield' of >95 percent.

The principal purpose of this document is, therefore, to provide guidance regarding the optimum techniques for adding FeNb to steel, in order to maximize recovery and minimize any variability in niobium levels in the final product.

The Addition of Niobium to Steels

Ladle Steelmaking and Chemistry

Niobium is typically added to steel in the form of FeNb (Figure 1). The particle size range can be varied to meet specific customer demands [1] depending on steel type and steelmaking route.

Figure 1. Particles of ferroniobium.

As revealed by the Ellingham diagram [2] in Figure 2, niobium's affinity for oxygen is lower than that of other microalloying additions such as vanadium and titanium, as well as the conventional steelmaking deoxidizers aluminum, silicon, and even manganese.
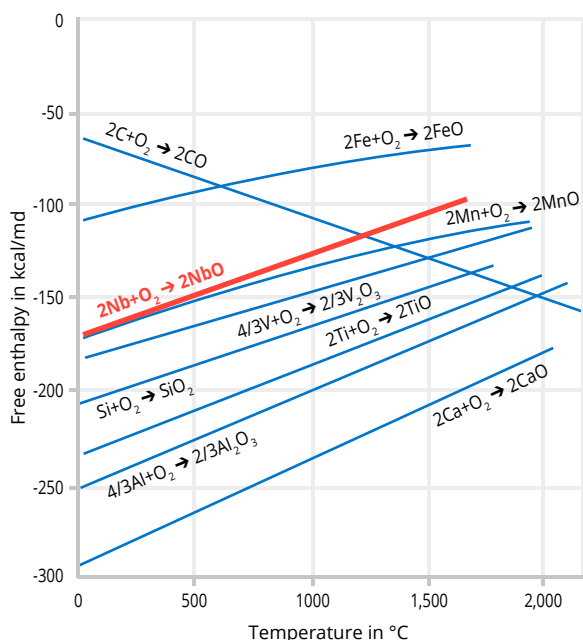

Figure 2. Ellingham diagram showing relative stabilities of different oxides [2].

Nevertheless, niobium will form oxides, which could render it ineffective during subsequent steel processing. FeNb should not be added during primary steelmaking when the oxygen is high, but in the ladle after the steel has been killed. This approach to the introduction of key elements through metallurgical reactions in the ladle is common practice in the majority of melting shops and makes practical and economic sense. It also leads to enhanced recovery rates of the elements in question.

Minimizing the Loss of Niobium by Reaction with Oxygen

Oxidation of niobium can occur by reaction with dissolved oxygen or with the slag. To minimize the former, the deoxidants, such as aluminum and silicon, should be added early in the tapping process, and well before the FeNb.

If the niobium comes into contact with the slag, it can be readily oxidized and removed from the liquid steel. For this reason, any interaction of the slag with the FeNb must be carefully minimized.

Mixing of the FeNb with the slag can be increased if the fluidity of the slag is high and this depends on the slag composition, the temperature of the melt and the oxygen content. The problem may be exacerbated by failure of the FeNb particles to penetrate the liquid steel to a sufficient depth after addition.

For steel produced by Basic Oxygen Furnace (BOF) Steelmaking, the oxygen content when the steel is tapped is higher than for Electric Arc Furnace (EAF) Steelmaking. Because of this, the fluidity of the slag tends to be higher for BOF steel, which can lead to more slag carryover into the ladle. Thus, the potential for mixing of slag and liquid steel is greater for steel produced by the BOF route. Regardless of the primary steelmaking process (BOF or EAF), slag carryover from the primary metallurgical vessel into the ladle is harmful for the production of clean steel and should be minimized.

Other factors which modify the flow characteristics during tapping can also affect slag/liquid steel mixing, for example worn tap holes.

This is a complex but important area of concern and one of the potential pitfalls for inexperienced operators to be wary of. Minimizing the loss of niobium by unwanted oxidation is central to the success of ladle addition techniques.

Physical Factors

As noted in the previous section, the potential loss of niobium through oxidation is an important factor, but there are also physical factors that can create barriers to optimum niobium recovery. These are the inability to successfully deliver the FeNb particles into the liquid steel and the incomplete dissolution of the FeNb particles themselves.

Delivering FeNb Particles into the Liquid Steel

The density of FeNb [3] is about 8,1 g/cm^3 compared to 7,1 g/cm^3 for liquid steel. So, without adequate stirring, the FeNb particles will tend to sink in the melt.

To minimize niobium losses, the FeNb particles should enter the liquid steel and dissolve fully. To facilitate this, an eye can be opened in any slag cover [4], to allow the FeNb particles to pass unhindered into the liquid steel (Figure 3). It is important that the eye is sufficiently large to allow the FeNb particles to enter the steel without being trapped by the slag. Stirring using argon gas or electromagnetic stirrers promotes mixing of the FeNb and liquid steel.
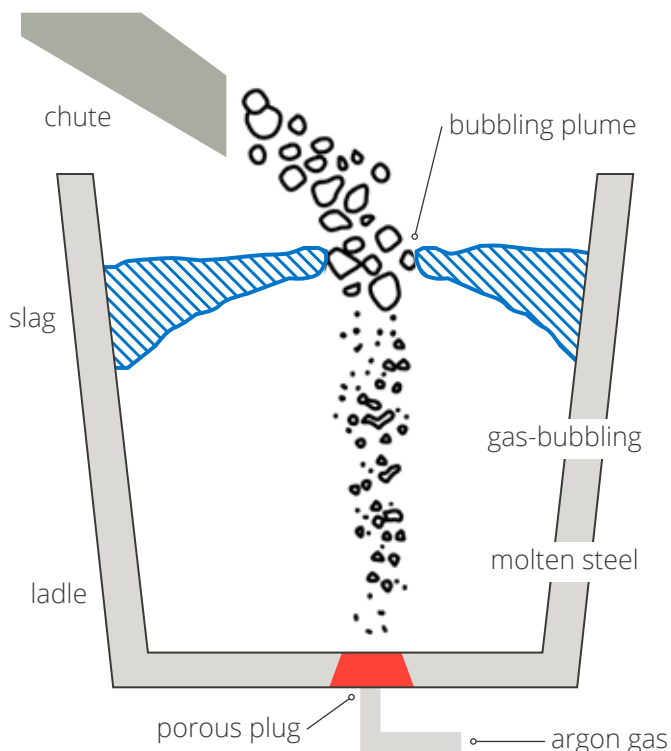
Smaller particles may be carried away by the strong convection currents associated with the high temperatures of the materials in the ladle. Exhaustion systems for dust collecting can also drag fine particles into the de-dusting system preventing them getting into the ladle. This is critical if the dust collector tubing is close to the alloy addition chute. Typically, particle size distribution from 5 to 50 mm can produce optimum yield. Addition in cans or cored wire can also avoid the risk of loss of FeNb, when using particle sizes below 5 mm.

Ensuring Delivery of the FeNb Particles into the Liquid Steel to a Depth which Minimizes Interaction with the Slag

During bulk steel production, FeNb particles are normally delivered to the liquid steel in the ladle via some form of chute.

The chute should be free from obstructions and the geometry and surface finish must be such that the FeNb particles enter the liquid steel with sufficient velocity to reach a depth below the surface, which minimizes interaction with the slag before they have sufficient time to dissolve.

Maximizing Dissolution of the FeNb Particles

The melting point of niobium, 2.477 °C, is much higher than that of iron, 1.538 °C. The addition of iron significantly reduces the melting point, reaching a minimum of 1.370 °C at about 15 wt.%Nb [5], Figure 4. Table 1 presents the chemical specification of standard FeNb (CBMM Spec. 111). It has a minimum of 63,5 wt.%Nb, giving a region of eutectic reaction around 1.500 °C. CBMM can also provide other specifications to meet the individual needs of customers.

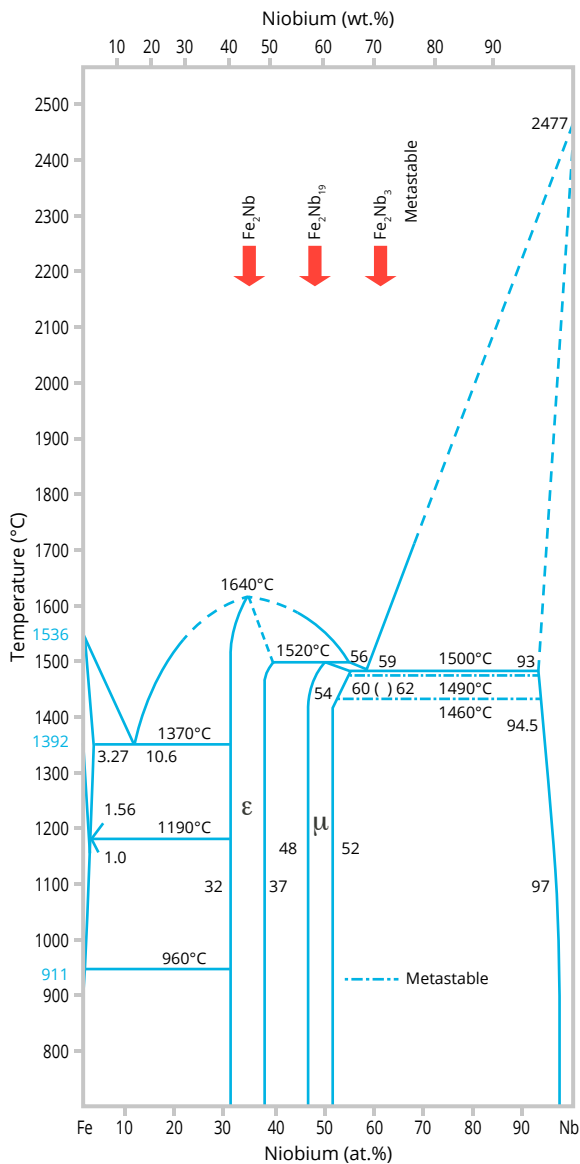*Figure 3. Schematic of a delivery system for FeNb particles to the ladle [4].*

chute · bubbling plume · slag · gas-bubbling · molten steel · ladle · porous plug · argon gas

Figure 4. FeNb phase diagram adapted from Zelaya-Bejarano [5].

Figure 5. Typical microstructure of standard FeNb ingots by SEM images [6].

Region	Phase	Atomic %					
		Al	Si	Ti	Mn	Fe	Nb
Needles (μ)	$Fe_{21}Nb_{19}$ (primary)	2,2 ±0,3	3,2 ±0,6	0,9 ±0,1	0,8 ±0,1	43,5 ±,8	49,4 ±0,6
Eutectic (e)	$Fe_{21}Nb_{19}$ (eutectic)	2,0 ±0,3	1,2 ±0,7	1,5 ±0,3	0,8 ±0,1	43,8 ±1,0	50,5 ±0,5
	Niobium (eutectic)	0,8 ±0,2	0,0 ±0,0	1,5 ±0,3	0,3 ±0,1	6,2 ±0.6	91,3 ±0.6
	Fe_2Nb_3 (eutectic)	1,6 ±0.3	1,0 ±0.3	1,9 ±0,4	0,7 ±0.1	36,5 ±0,5	58,3 ±0,4

Table 2. Chemical Composition of the Main Phases in Standard FeNb Ingots [6].

Ferroniobium Standard Chemical Specification (wt.%)							
Nb	Si	Al	P	C	S	Ta	Fe
63,5 min.	3,0 max.	2,0 max.	0,22 max.	0,20 max.	0,04 max.	0,20 max.	balance

Table 1. Chemical Specification of Standard FeNb (CBMM Spec. 111 ver. 6.0).

Figure 5 shows the microstructure of FeNb characterized using scanning electron microscopy and energy dispersive spectroscopy. It comprises of two predominant regions: primary laths of the intermetallic $Fe_{21}Nb_{19}$ (μ) and eutectic zones. The eutectic zones are formed by three phases: (e1) $Fe_{21}Nb_{19}$, (e2) niobium globules and (e3) Fe_2Nb_3. The chemical compositions of the main phases are shown in Table 2.
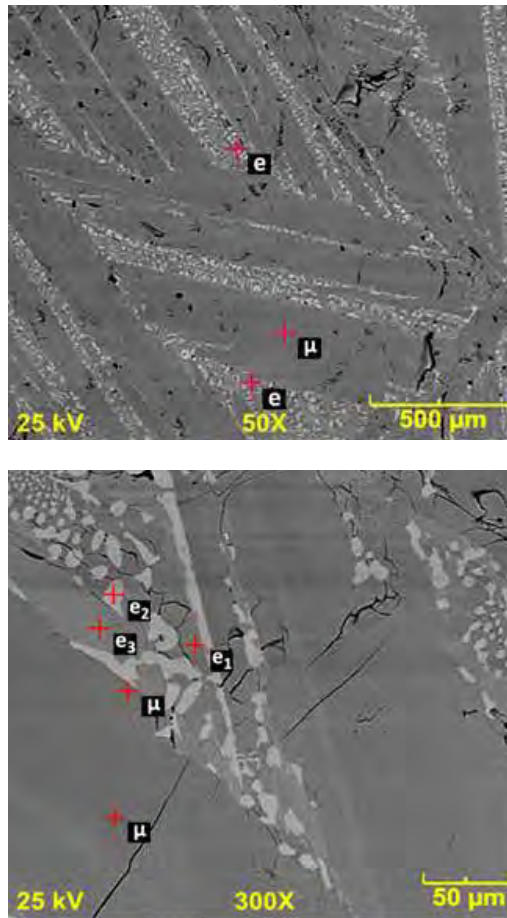
The primary laths melt from 1.575 °C to 1.530 °C while the eutectic melts from 1510 °C to 1.500 °C [6].

The dissolution of FeNb particles involves three distinct stages as shown in the model below (Figure 6) [5,6].
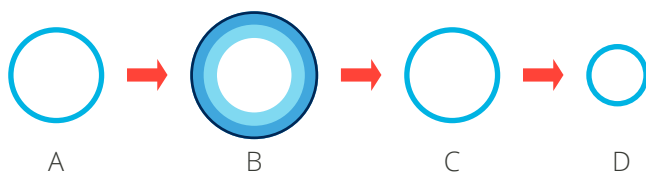

Figure 6. Model for dissolution of standard FeNb particles in liquid.

1st stage (A→B): Soon after the particles at room temperature are added to the steel bath at steelmaking temperatures of around 1.600 °C, they heat up and begin to locally freeze the liquid steel, which forms a solidified steel shell around them (B);

2nd stage (B→C): The steel shell achieves a maximum thickness when its temperature equals the steel liquidus temperature and it begins to remelt. Even before the remelting of the shell begins, the FeNb particles achieve temperatures higher than 1.500 °C, when the eutectic regions melt down and begin to react with iron, thereby forming a reaction layer below the frozen steel shell. Immediately after the complete remelting of the steel shell, the partially melted FeNb particle comes into direct contact with the liquid steel;

3rd stage (C→D): In this step, the dissolution itself occurs through a combined mechanism of melting and liquid/solid diffusion of the FeNb particles. The usual steelmaking temperatures of around 1.600 °C are even higher than the liquidus temperature of the primary laths of the intermetallic $Fe_{21}Nb_{19}$, ie 1.575 °C. So, even the remaining primary laths of $Fe_{21}Nb_{19}$ (μ) can be melted during this process.

Stirring and or gas bubbling (introducing dynamic conditions) will significantly shorten dissolution times but over-aggressive stirring must be avoided in order not to disturb the slag metal interface layer.

In some special circumstances, FeNb additions can also be made using a cored wire filled with very fine particles <2 mm diameter and when this technique is used with vacuum processes, for example with RH degassers, niobium recoveries of close to 100 percent are possible.

The successful dissolution of FeNb particles depends on a range of factors:

1. The temperature of the liquid steel.
The higher the temperature, the more rapid is the dissolution rate.

2. The time allowed for dissolution.
As well as the steel temperature, this also depends on the size of the FeNb particles.

3. The degree of agitation of the liquid steel.
More rapid agitation will increase dissolution rates but the agitation must not be too vigorous as this may cause losses to the slag.

Where lower than expected niobium recoveries are experienced, trials can be carried out using repeated sampling to determine the time required for complete dissolution of FeNb under normal plant operating conditions.

Checklist to Maximise Niobium Recovery in Steel Production

Based on the above considerations, the following strategy should be adopted to maximize niobium recoveries:

o Select a grade of FeNb with particle sizes small enough to allow dissolution under normal plant operating conditions, but which are not too small to cause significant losses due to strong convection currents in the air or slag entrapment. Typically, a particle size distribution from 5 to 50 mm can produce optimum yield. Addition in cans or cored wire can also avoid the risk of loss of FeNb, when using a particle size below 5 mm.

o Although niobium is not as reactive with oxygen as other elements Al, Si and Ti, the addition of FeNb should take place after the complete deoxidation of the steel bath, in order to prevent niobium losses by oxidation.

o Stirring by argon bubbling should be adopted to accelerate the dissolution of FeNb particles, prevent large particles from settling in the bottom of the ladle, and promote a small, slag-free surface to avoid FeNb losses by entrapment in the slag. After the addition of standard FeNb particles, argon bubbling from 10 to 15 minutes is recommended for the complete dissolution of FeNb.

o Make the FeNb addition after the primary deoxidizers, such as aluminum and silicon, which should be added early in the tapping sequence.

o During tapping, add FeNb to the ladle when it is between about 30-60 percent full. Additions made too early may increase losses by oxidation and additions too late may not allow sufficient time for complete dissolution.

o Ensure that the delivery system can introduce the FeNb particles to the ladle with sufficient velocity to allow them to go well below the surface of the steel to minimize interaction with the slag.

o Ensure that the eye opened in the slag cover is sufficiently large so that during addition the FeNb is not captured by the slag.

o Ensure that the steel temperature, the time and degree of agitation allow complete dissolution of the FeNb particles prior to casting. The dissolution time can be determined by trials involving repeated sampling and measuring the time at which the niobium content becomes constant.

If this checklist is followed, it should be possible to obtain high, consistent recoveries of niobium in excess of 95 percent. However, if problems still persist, additional advice can be obtained from www.cbmm.com and, if required, experts from CBMM can visit individual clients to provide on-site support.

References

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Technical content prepared by
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