

FERRONIUM ALLOYING TECHNIQUES IN IRON & STEEL MAKING

PHYSICAL PROPERTIES OF FERRONIUM

Niobium alloying in iron and steel materials is done in most applications by adding ferroniobium into molten iron during secondary metallurgical treatment in a ladle [1]. Ferroniobium is typically produced by reducing niobium oxide concentrate and iron ore with aluminium in an electric arc furnace (aluminothermic reduction process) [2]. The liquid ferroniobium is cast into moulds and the solidified ingots are subsequently crushed into smaller fractions that are sieved into various lump size distributions.

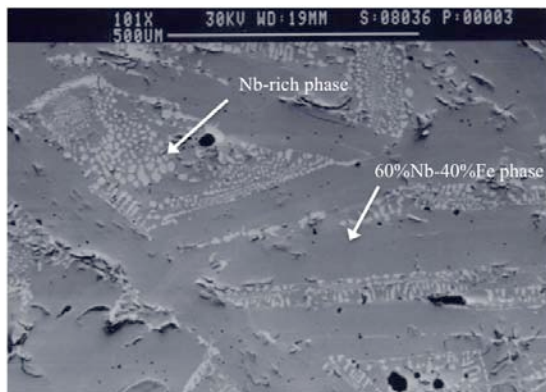


Figure 1: SEM micrograph of a 66%Nb ferroalloy.

According to the binary Fe-Nb phase diagram a 66%Nb ferroalloy composes of svariious phases as shown in Figure 1. The matrix consists of the intermetallic μ -phase ($Fe_{21}Nb_{19}$) containing approximately 60 mass percent Nb. The brittle μ -phase forming the bulk of the ferroalloy facilitates crushing of the cast ingots into smaller fractions. Embedded niobium-rich islands contain more than 95 mass percent Nb. The melting points of these phases are rather different resulting in a melting range of the ferroalloy from around 1550°C to more than 1800°C. Thus ferroniobium is a class-II ferroalloy that does not melt when added to liquid iron but rather dissolves [4-6]. There is no exothermic reaction between ferroniobium and liquid iron.

According to Figure 2, two kinetic steps determine the total dissolution time of a class-II ferroalloy. As the ferroalloy has ambient temperature before entering the melt (A), a steel shell solidifies around it after entering the melt (B). Inside this steel shell the agent heats up before the steel shell re-melts (C) and finally dissolution of ferroniobium takes

place (D-E). Thus, shell formation delays the actual dissolution process, which is based on diffusion processes between solid ferroniobium and liquid iron.

In general and for a given total mass, finer lump size results in a larger total surface between ferroalloy and bath leading to a faster dissolution process. Smaller lumps also have a lower heat capacity and thus reduce the shell period. Since ferroniobium has a higher specific weight than liquid iron it tends to sink to the bottom of the ladle and should hence not be too large in size for an optimised mixing-process. On the other hand, with finer ferroniobium size distributions dust loss can become significant and the risk of entrapment in the ladle slag is increased. The dusting and slag entrapment problem can be avoided when fine ferroniobium is applied by cored wire feeding.

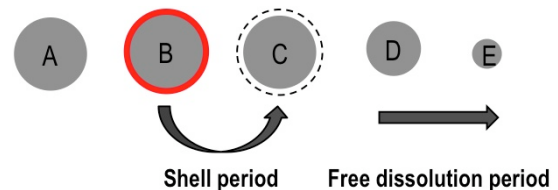


Figure 2: Kinetic steps determining ferroniobium dissolution.

The bath temperature controls the mass flux during the free dissolution period (Figure 3). Agitation of the melt increases the mass flux considerably [4].

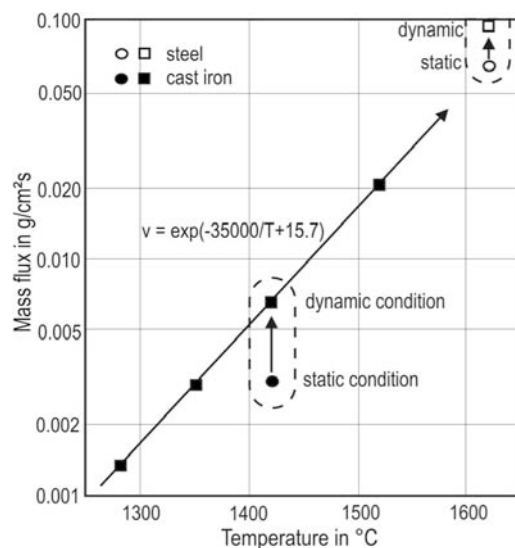


Figure 3: Experimentally determined mass flux for ferroniobium in iron and steel melts.

The free dissolution period ($t_{diss.}$) can be calculated using the density of ferroniobium ($\rho = 8.1 \text{ g/cm}^3$), the mass flux (v) according to Figure 3, and the lump diameter (d) as follows:

$$t_{diss.} = \frac{\rho}{2 \cdot v} d \quad (1)$$

The shell period, which is in the order of a few ten seconds in steel, has to be added to the result of equation 1 to obtain the total mixing time. Accordingly, the total mixing time of ferroniobium in liquid steel is usually below 300 seconds whereas in cast iron it can take much longer.

ALLOYING STRATEGIES IN STEEL

The affinity of niobium to oxygen is much lower than that of other microalloying elements and even that of manganese (Figure 4). When ferroniobium is added to fully killed steel after bulk alloying one obtains an excellent the recovery rate of typically above 95% and particularly narrow scattering around the targeted alloying content.

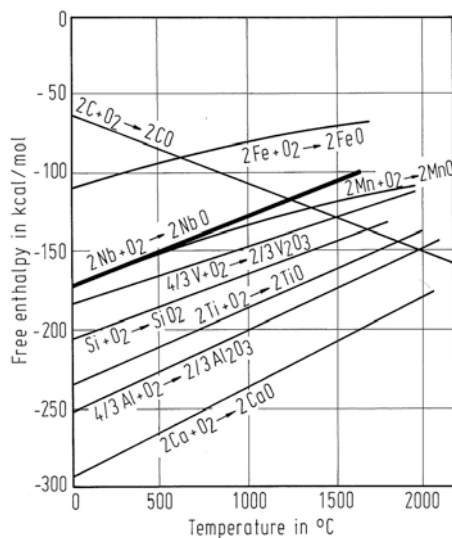


Figure 4: Free reaction enthalpy of various ferroalloys.

Dumping of ferroniobium from big bags into a ladle with argon gas stirring is common alloying practice method. The addition should be made above the bare spot as to avoid trapping of ferroalloy in the slag layer. With only one active plug, the alloy addition should be made in the main melt circulation plane, preferably above the plug [7]. This plane is defined by the ladle axis and the eccentric plug position. With centric alloy addition, the plug position is of minor importance. An increased stir gas flow rate results in an acceleration of the mixing-process, indicated by a shorter total mixing time. Figure 5 represents the mixing behaviour of ferroniobium with regard to lump size and stir gas flow rate.

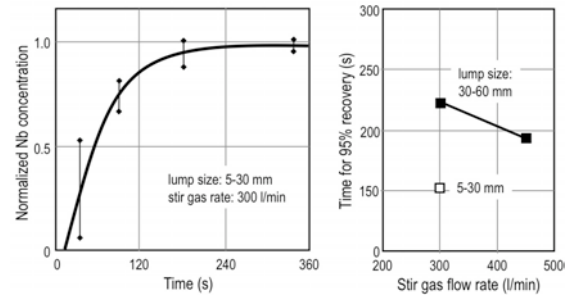


Figure 5: Mixing behaviour of ferroniobium in a large ladle with argon stirring (after [7]).

With cored wire or injection feeding, both, feeding location and plug position, have only minor influence on the required mixing-time, as the time for ferroniobium dissolution due to small lump size is very short. Yet, increasing the wire feeding speed can significantly accelerate the mixing process.

From an economical point of view, alloying by cored wire is only attractive when the recovery of bulk ferroniobium is below 90%.

Adding ferroniobium via the CAS process results in very high recovery since no slag layer covers the liquid bath that could lead to trapping of alloying agent. The argon atmosphere also prevents any ferroniobium loss due to oxidation. In this respect very precise alloying is possible by the CAS process as shown in Figure 6.

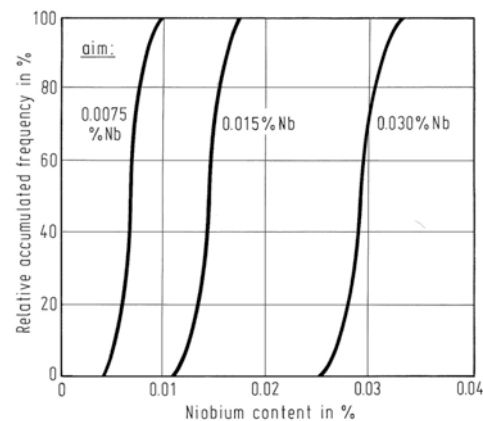


Figure 6: Scattering range of niobium content in micro-alloyed steel over a three-months production period [8].

In the production of the Nb-bearing extra-low carbon steel or Nb-bearing low alloy steel with low [H], small-sized ferroniobium can be added directly onto the molten steel surface in the RH vessel after RH treatment with no mechanical loss, achieving a ferroniobium recovery ratio of 95% or more. The stirring intensity is higher in the RH vessel than in ladles with argon gas bubbling. Therefore, larger-sized ferroniobium can be used in the RH vessel.

Dusting loss is also less in comparison with ladle addition with gas bubbling.

ALLOYING STRATEGIES IN CAST IRON

The different mechanism of ferroniobium dissolution in high carbon iron as compared to low carbon steel has an effect on the kinetics of this process. Both, the lower mass flux rate (Figure 3) as well as the relatively low bath temperature explain the fact that ferroniobium dissolves only slowly.

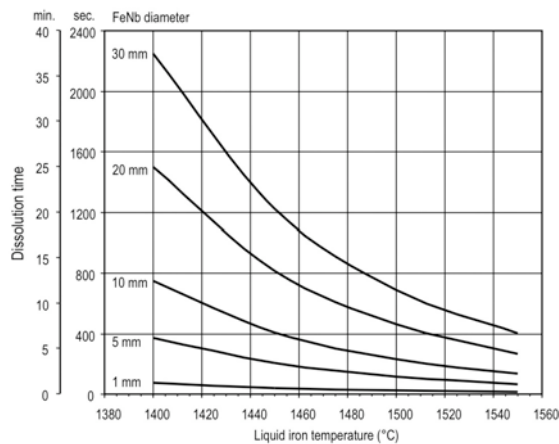


Figure 7: Dissolution time of ferroniobium in eutectic iron (4.23 %C).

Figure 7 shows the calculated time required for complete dissolution in function of ferroniobium lump diameter. Some turbulence in the molten bath, which can be obtained by stirring or injection, improves the dissolution kinetics.

Considering a typical melt temperature of 1400°C in a foundry, Figure 7 predicts a mixing period of approximately 15 minutes for dissolution of a ferroniobium lump size of 12 mm (~1/2 inch). Several methods have been developed to alloy ferroniobium in a practical way:

- Lump type ferroniobium is charged together with solid scrap into the melting furnace, thus allowing for a long dissolution period. This option is particularly applicable when the furnace is constantly producing Nb-alloyed iron. In a mixed operation, several purging melts would be necessary to remove Nb traces.
- Addition during tapping provides a relatively short time window for dissolution, thus rather fine-grained ferroniobium has to be used dissolving within a few minutes. Accordingly, many foundries prefer a size distribution of 1-3 mm.
- A very effective alloying method is injection of ferroniobium fines by cored wire. The fine particle size enables efficient dissolution. The

addition of exothermic agents into the cored wire can further accelerate the dissolution by bath turbulence and a temperature increase [9].

- Superheating of the melt in a holding furnace is an alternative means to overcome poor recovery (Figure 8). A proven practice is to hold a melt that is richer in Nb-alloying than the final target and to mix it with an appropriate amount of unalloyed iron in a transfer ladle.

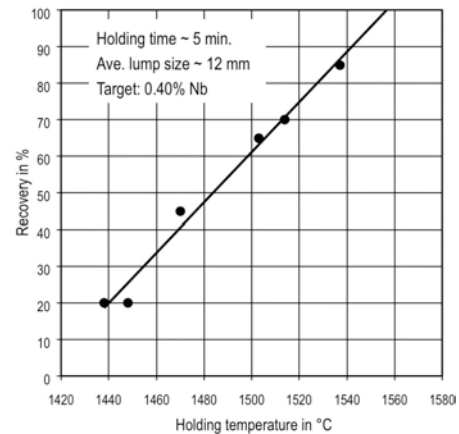


Figure 8: Recovery of ferroniobium in eutectic iron during isothermal holding.

CBMM SUPPLY SPECTRUM OF FERRO-NIOBIUM

CBMM supplies ferroniobium in a variety of specifications concerning purity, lump size, and packaging to meet the individual needs of customers. Three ferroniobium specifications are available from CBMM:

- Standard grade ferroniobium (FeNb STD 111) is used primarily in carbon steel making and accounts for the majority of applications.
- Vacuum grade FeNb VG 211 contains restricted amounts of Ta, Si, Ti, O, N, P, C, S, Pb and Sn and is recommended for steel grades being produced in special furnaces, including vacuum induction furnaces.
- FeNb STD 113 Stainless Steel Grade comprises reduced trace elements such as Al, Sn, P and Pb as these elements can impair high-temperature properties like creep and ductility in certain stainless steel grades.

For typical applications of ferroniobium standard grade (STD 111) in carbon steel the intake of phosphorous and sulphur is always less than 6 and 3 ppm, respectively.

Each chemical specification is available in various lump size distributions and packages. Ferroniobium supplied by CBMM consists of max 10% undersize, but no fines.

| CBMM chemical specification in weight % | | | |
|---|-----------------------|--------------------------|------------------------------------|
| Element | FeNb Standard STD 111 | FeNb vacuum grade VG 211 | FeNb Stainless Steel Grade SSG 113 |
| Nb | 63.0 min. | 63.0 min | 63.0 min. |
| Ta | 0.2 max. | 0.2 max. | 0.2 max. |
| Si | 3.0 max. | 0.3 max. | 3.0 max. |
| Al | 2.0 max. | 0.15 max. | 1.0 max. |
| P | 0.2 max. | 0.01max. | 0.1 max. |
| C | 0.2 max. | 0.05 max. | 0.1 max. |
| S | 0.1 max. | 0.01 max. | 0.1 max. |
| Ti | - | 0.10 max | 0.5 max. |
| Pb | - | 0.0050 max. | 0.05 max. |
| Sn | - | 0.0050 max. | 0.1 max. |
| N | - | 0.030 max. | 0.1 max. |
| H | - | - | 0.02 max. |
| Co | - | - | 0.05 max. |
| O | - | 0.1 max. | - |
| Fe | Balance | Balance | Balance |

| Typical FeNb Particle Size Distribution, Bulk Density and Packages | | | |
|--|-----------------------------|--|--|
| Description | Size distribution in mm (*) | Bulk density in g/cm ³ (**) | Available packaging and shipment weight |
| Coarse | 10 – 50 | | Big bag: 1 ton Drum: 250 kg |
| | 5 – 50 | | |
| Medium | 10 – 30 | | Big bag: 1 ton Drum: 250 kg Can: 10 lbs, 25 lbs, 10 kg |
| | 3 – 15 | | |
| | 1 – 12.5 | | |
| | 2 – 10 | | |
| Fine | < 2 | | |

(*) Maximum tolerances for over and undersize conform international standards.
(**) Small bags also can be supplied under special order.

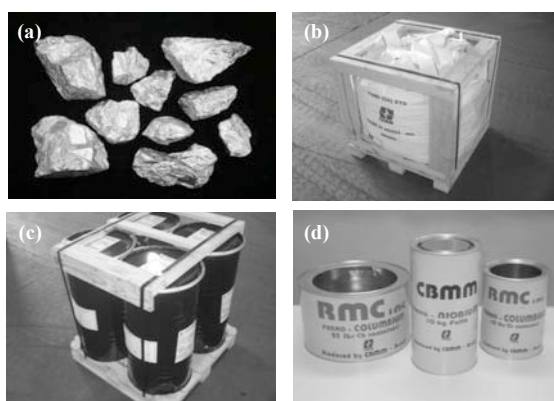


Figure 9: Ferroniobium lumps (a) packed in big bag (b), drum (c) and can (d).

Quality control of the ferroniobium lots is done according to ISO 4552-2:1987 (Ferroalloys - Sampling and Sample Preparation for Chemical Analysis - Part 2: Ferrotitanium, ferromolybdenum,

ferrotungsten, ferroniobium, ferrovanadium) by automatic sampling. The sieve analysis is carried out following an internal CBMM procedure based on the international Standard ISO 4551:1987 (Ferroalloys - sampling and sieve analysis).

CBMM is ISO 9001 certified since 1994.

LITERATURE REFERENCES

1. A.T. Peters, "Metallurgical Factors in Ferroalloy Selection", I&SM Journal, January 1977, p. 26.
2. C. A. Sousa: "The Evolution of FeNb Manufacturing", Niobium 2001 – Science & Technology, TMS 2001, p. 89.
3. J.M.Z. Bejarano et al.: "The Iron – Niobium Phase Diagram", Z. Metallkunde. 84, 1993.
4. P.G. Sismanis et al.: "The dissolution of Nb, B and Zr Ferroalloys in Liquid Steel and Liquid Iron", I&SM Journal, July 1989, p. 39.
5. S.A. Argyropoulos: "On the Recovery and Solution Rate of Ferroalloys", I&SM Journal, May 1990, p. 77.
6. S. A. Argyropoulos and P.G. Sismanis: "The Mass Transfer Kinetics of Niobium Solution into Liquid Steel, Metallurgical Transactions B, Vol. 22B, August 1991, p. 417.
7. K. Marx, et al.: "Advanced Strategies for Alloying Processes in Steelmaking Ladles", Proc. of 5th European Oxygen Steelmaking Conference, Aachen 2006, p. 312.
8. A. Bergman et al.: Steel Time, June 1988, p. 46.
9. J. Schade et al.: "Cored-Wire Microexothermic Alloys for Tundish Metallurgy", I&SM Journal, January 1990, p. 53.