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DISSOLUTION OF FeNb IN LIQUID STEEL

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Abstract

Niobium is a well-established microalloying element for the production of High-Strength Low-Alloy (HSLA) steels and it is usually added in amounts smaller than 0.10% in the form of standard ferroniobium (FeNb) [1]. The operational practice at the melt shop, as well as controlled dissolution trials in the laboratory and on an industrial scale, have shown that standard FeNb dissolves very rapidly and with high recovery yields. It was verified that the addition of FeNb requires good control of some parameters, such as deoxidation temperature, stirring time and particle size. For each application, CBMM produces lumpy material in a wide range of size distributions. Taking advantage of using very fine particles, recently CBMM has developed a new briquetting process in order to agglomerate FeNb fines smaller than 2 mm to make them robust enough for easy handling during their addition to the molten steel. This paper aims at presenting a review of the FeNb characterization, the dissolution rate of lumpy and briquetted fines, as well as showing the mechanism of dissolution at the FeNb/steel interface. In the laboratory trials it was observed that briquetted FeNb fines dissolve faster than the lumpy material at temperatures of 1560 °C, 1600 °C and 1640 °C. It was verified that the difference between the dissolution rate of FeNb briquettes and lumpy material is less significant for higher temperatures (1640 °C). The industrial trials showed that the complete dissolution of briquettes and lumpy material occurred in less than 10 minutes at 1570 °C and that the yield of the niobium addition was higher than 98% for both materials.

Introduction

Niobium is a well-established microalloying element for the production of HSLA steels and it is usually added in amounts smaller than 0.10% in the form of standard FeNb [1]. The operational practice at the melt shop, as well as controlled dissolution trials in the laboratory and on an industrial scale have shown that standard FeNb dissolves very rapidly and with high recovery yields. It was verified that the addition of FeNb requires a good control of some parameters, such as deoxidation temperature, stirring time and particle size, as is the case for all alloy additions in general. For each application, CBMM produces lumpy material in a wide range of size distributions. Taking advantage of using very fine particles, recently CBMM has developed a new briquetting process in order to agglomerate FeNb fines, smaller than 2 mm, to make them robust enough for easy handling during their addition to the molten steel.

This paper presents a review of the FeNb characterization, the dissolution rate of lumpy and briquetted fines, as well as showing the mechanism of dissolution at the FeNb/steel interface.

Characterization of Standard FeNb

As can be seen in Figure 1(a), standard FeNb is a high-niobium alloy containing approximately 65 wt.% niobium [2]. Its microstructure consists of two predominant zones: (a) primary laths of the intermetallic $Fe_{21}Nb_{19}$ (μ) and (b) eutectic zones (e). The eutectic zones are in turn formed by the following stable phases: (e_1) $Fe_{21}Nb_{19}$ and (e_2), terminal globules of high content, as well as a third metastable phase Fe_2Nb_3 (e_3), Figure 1(b) [3,4].

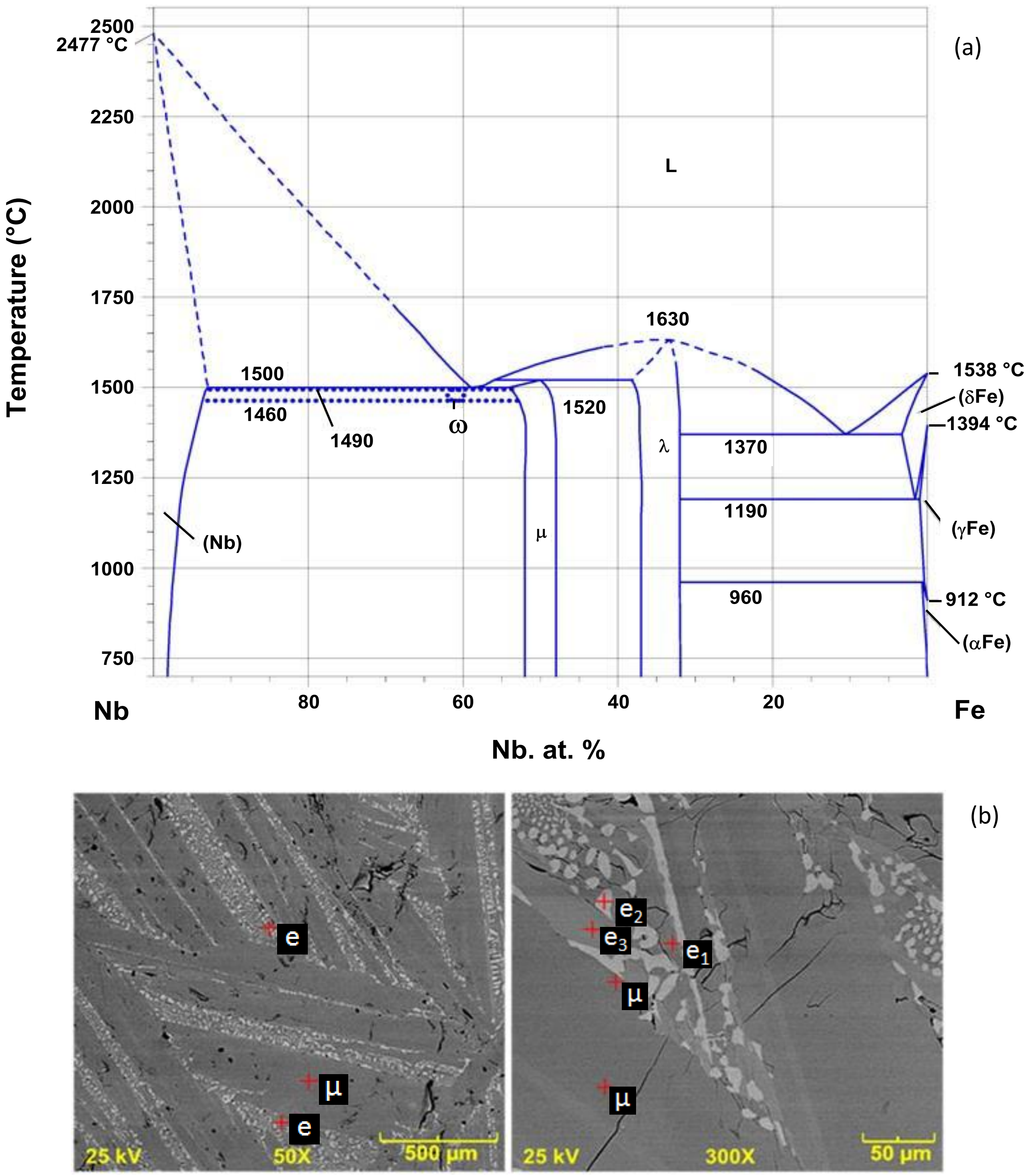


Figure 1. FeNb phase diagram according to Zelaya-Bejarano [2] (a) and typical microstructure of standard FeNb (b) [3,4].

Dissolution of Standard FeNb

In order to study the dissolution rate of briquetted FeNb fines (<2 mm) and lumpy material (20, 30 and 40 mm in equivalent diameter), laboratory and industrial comparative dissolution trials were carried out by addition of these particles to steel baths at temperatures between 1560 and 1640 °C. The appearance of the briquettes and lumps is shown in Figure 2. The binder used for briquetting was an inorganic silicate based material.

The laboratory trials were carried out in an induction furnace by dropping the briquettes or lumps on the surface of deoxidized low carbon steel baths (35 kg) heated up to 1560, 1600 and 1640 °C. Samples of liquid metal were taken by suction into quartz tubes in order to follow the niobium increase in the steel bath during the dissolution process.

The industrial trials were carried out by simple dropping of FeNb briquettes or lumps on steel baths at 1570 °C contained in a 70 ton ladle. The lumpy material comprised particles with size distributions from 5 to 15 mm and from 15 to 30 mm. The briquettes were 40 mm in equivalent diameter. The metallic charge was melted down in an electric arc furnace and then poured into the ladle for manganese, silicon and aluminum deoxidation to achieve an active oxygen content below 20 ppm. Samples were taken during the heats and the temperature was adjusted in accordance with standard procedures for steel casting.

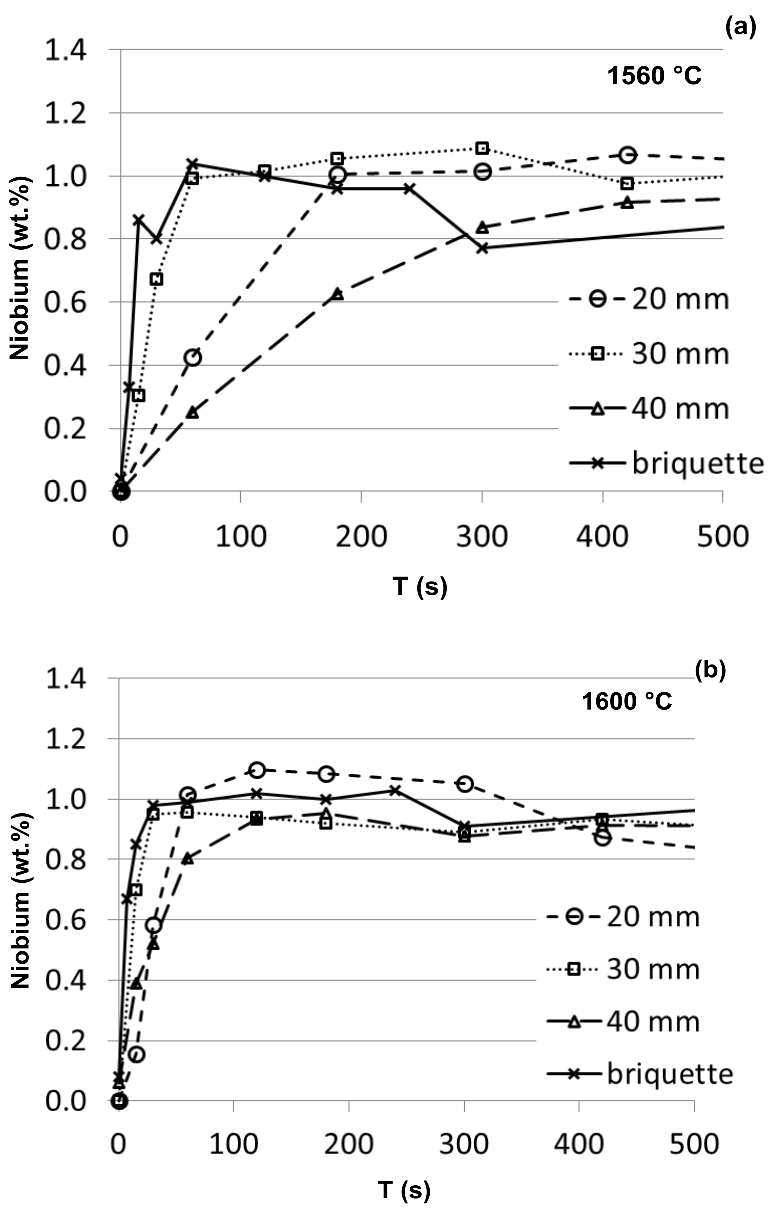
Figure 2. FeNb lump (top) and briquette (bottom).

With the aim of describing the dissolution mechanism at the interface between the briquettes or lumps and the steel bath, six interrupted dissolution trials were also carried out in a laboratory scale induction furnace. For this purpose, the particles were partially immersed in the steel baths at 1550 °C, 1600 °C and 1650 °C, held in for 10 seconds and then water quenched for metallographic analysis.

Results

The results of the laboratory scale and industrial dissolution trials are shown in Figures 3 and 4 respectively in terms of the increase of niobium content in the steel bath during the heats.

In Figure 3 it is possible to observe that the dissolution of FeNb briquettes was faster than the dissolution of lumpy material for all the temperatures established for the trials. However, the difference between the dissolution rate of FeNb briquettes and lumpy material was less significant for higher temperatures. For both, the dissolution rate increased by increasing the bath temperature from 1560 °C up to 1640 °C. It was noticed that briquettes and lumps dissolved in less than 1 minute at the highest temperature (1640 °C). As in previous work [3,4], it was verified that the dissolution rate of lumpy material increases by decreasing the particle size.



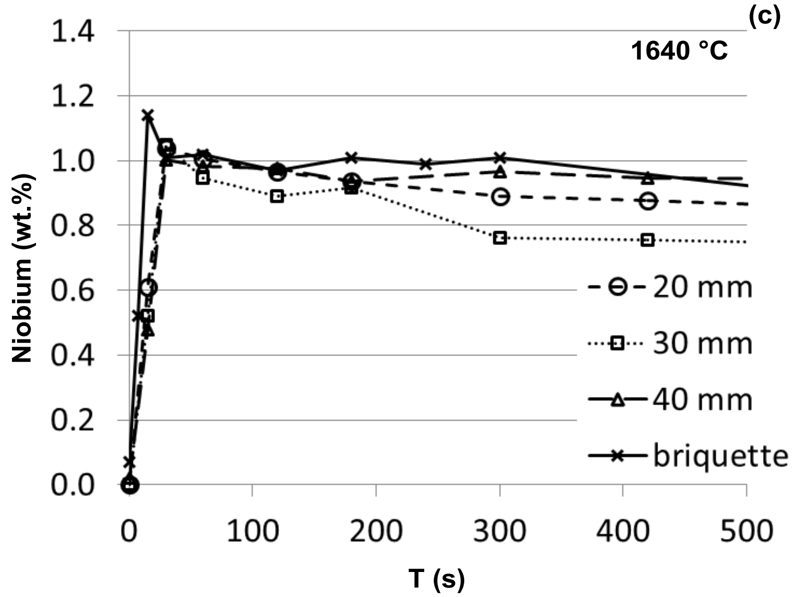


Figure 3. Niobium content as a function of time during the dissolution of FeNb briquettes and lumps at; (a) 1560 °C, (b) 1600 °C and (c) 1640 °C (laboratory scale trials).

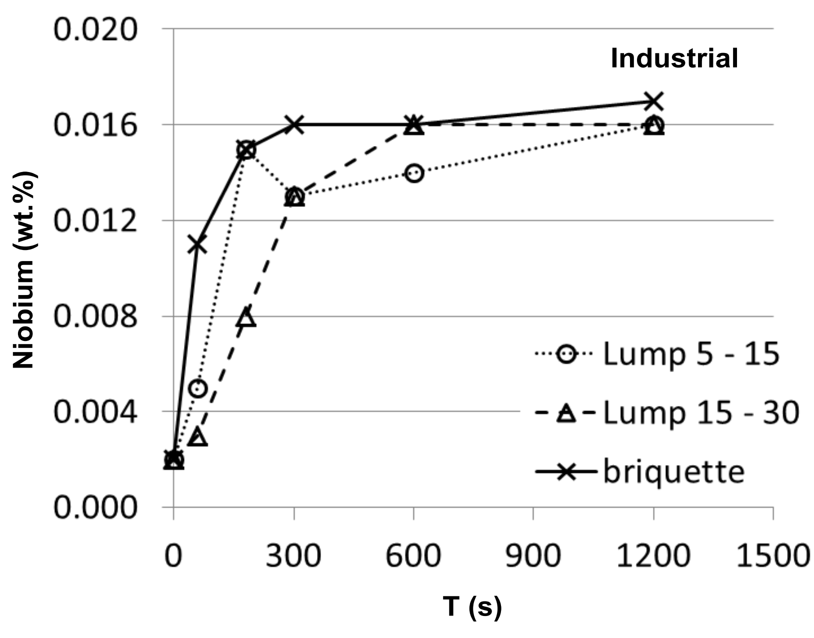
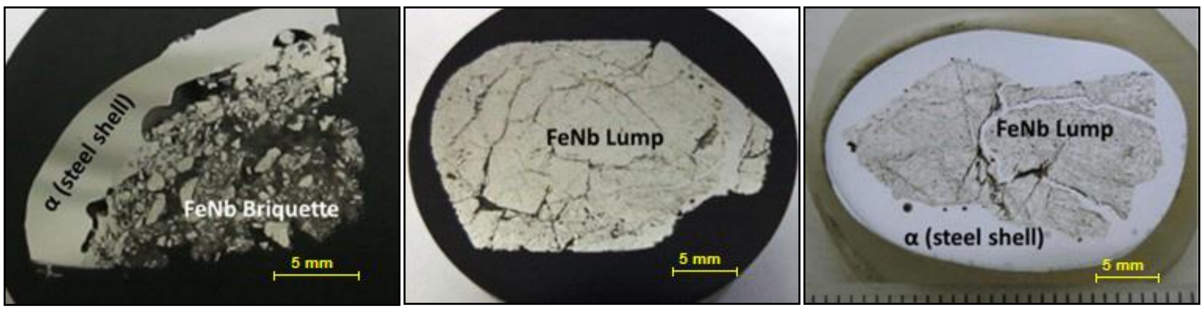


Figure 4. Niobium content as a function of time during the dissolution of FeNb briquettes and lumps at 1570 °C (industrial scale trials).

In Figure 4 it can be seen that in the industrial trials the dissolution rate of briquettes was higher than for lumpy material in the same way as was observed in the laboratory trials. The FeNb briquettes dissolved in less than 5 minutes at the temperature of 1570 °C. As was observed in the laboratory scale trials, the dissolution rate of the lumpy material increased by decreasing the particle size. The yield of the niobium addition at the steel shop was higher than 98% for briquettes and lumpy material.

In the interrupted dissolution trials, conducted at different temperatures, both briquettes and lumps formed a frozen steel shell around them, Figure 5. The thickness of the steel shell decreased as the bath temperature increased, Figures 5(b) and (c). At the interface, the briquettes presented a large number of small (bonded and loose) particles while the lumps consisted of bigger pieces, some of them with cracks filled by thin iron-rich threads.



FeNb Briquette – 1550 °C (a)   FeNb Lump – 1550 °C (b)   FeNb Lump – 1600 °C (c)

Figure 5. Steel frozen shells around the FeNb briquette and lump.

Figure 6 shows a microstructural view of the interface between the FeNb briquettes and lump and the steel bath at 1550 °C. The following regions can be recognized:

- The steel shell itself (α) was constituted by an iron-rich layer solidified around the briquettes or lumps during their immersion in the metal bath. The steel shell has the same composition as the steel bath;
- The reaction layer that propagates inwards into the briquette through the binder (b) or into the lump through pre-existing cracks (c). This reaction layer (e'+ α) is composed of an iron rich terminal phase (α) and a low niobium content eutectic zone (e');
- The core of the briquette or lump has the same chemical composition and micro-constituents as the original lumps or briquettes - primary laths of μ and the eutectic zones (e).

Briquette – 1550 °C (a) Lump – 1550 °C (b) Lump – 1550 °C (c)

Figure 6. Microstructure of FeNb briquettes and lump at the interface with the steel bath.

The aspect of the interface at 1600 °C and 1650 °C for both lump and briquette was similar, but the steel shell (α) was thinner than for 1550 °C. It was observed that for all the temperatures adopted for the tests, the briquetted FeNb fines, as well as the lumpy material, began to melt down within the eutectic zones.

Discussion

The faster dissolution of the briquettes in relation to the lumpy material, as shown in Figure 3, can be explained by the higher reaction surface area of FeNb fines that are readily released from the binder and immediately brought into contact with the liquid steel. In fact, in Figure 6 it is possible to observe that a large number of small loose FeNb particles are completely exposed in the reaction layer that was formed between the briquette and the steel bath. As soon as the inorganic binder melted down, the FeNb particles were released to the liquid steel and the silicate inclusions floated to the slag.

In Figure 6 it can also be observed that the briquetted FeNb fines, as well as the lumpy material, began to melt down within their eutectic zones. As is shown in the phase diagram in Figure 1, the eutectic zones begin to melt down at approximately 1500 °C, well below the typical steelmaking temperatures of about 1600 °C. The remaining primary laths of $Fe_{21}Nb_{19}$ (μ) melt down also below the typical steelmaking temperatures, when reaching the liquidus temperatures, between 1530 °C and 1570 °C. This behavior explains why both briquettes and lumps dissolve very quickly when added to the liquid steel bath at the melt shop.

As had been verified for lump FeNb [3,4], in the present work, it was possible to verify that the dissolution of briquetted fines occurs through the same mechanism, Figure 7:

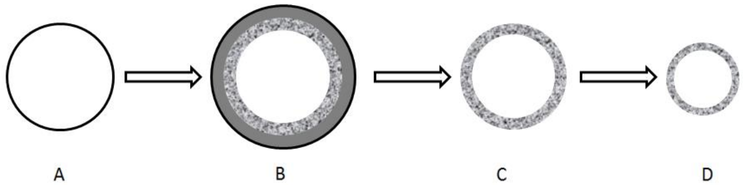


Figure 7. Mechanism of dissolution of FeNb particles in liquid steel.

1st stage (A→B): As soon as the particles at room temperature are added to the steel bath at steelmaking temperatures of around 1600 °C, they begin to heat up and locally freeze the liquid steel, forming a solidified steel shell around them;

2nd stage (B→C): The steel shell achieves its maximum thickness when the temperature equals the steel liquidus temperature and then it begins to remelt. Even before the remelting of the shell begins, the FeNb particles achieve temperatures higher than 1500 °C, whereupon the eutectic regions melt down and begin to react forming the reaction layer below the frozen steel shell, as shown in Figure 6. After the complete remelting of the steel shell, the partially melted FeNb particle comes into direct contact with the liquid steel leading to its rapid dissolution in the liquid. The rapid dissolution of the FeNb particles for all the temperatures adopted indicates that the remelting of the steel shell formed around the particle is not the controlling stage for the mechanism of dissolution;

3rd stage (C→D): In this stage, the dissolution occurs through a combined mechanism of melting and liquid/solid diffusion of the FeNb particles, both controlled by heat transfer.

The small difference between the dissolution rate of FeNb briquettes and lumpy material at higher temperatures (1600 °C and 1640 °C) can be explained by the fact that the effect of particle size is minimized when a higher superheat is applied to the steel bath as was shown by Webber [5]. At the higher temperatures the eutectic zones are quickly melted down at exposing the remaining primary laths of $Fe_{21}Nb_{19}$ (μ) phase to the melt.

The high and similar addition yields for both briquettes and lumpy material indicates that the differences in the dissolution rate are strictly related to kinetics once the FeNb particles have the same physicochemical properties.

Conclusions

1. In the laboratory trials it was observed that briquetted FeNb fines dissolve faster than the lumpy material at temperatures of 1560 °C, 1600 °C and 1640 °C. It was verified that the difference between the dissolution rate of FeNb briquettes and lumpy material is less significant at higher temperatures (1640 °C).

2. The industrial trials showed that the complete dissolution of briquettes and lumpy material occurred in less than 10 minutes at 1570 °C and that the yield of the niobium addition was higher than 98% for both materials.

3. The dissolution rate of FeNb briquettes and lumpy material increased by increasing the bath temperature.

4. Both briquettes and lumps initially formed a frozen steel shell around them. However, while lumpy material exhibited bigger pieces, the briquettes exhibited a large number of small loose FeNb particles at the interface, which may explain their higher dissolution rates.

5. The dissolution of FeNb briquettes and lumps occurs readily through a combined mechanism of melting and liquid/solid diffusion, both controlled by heat transfer.

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