# The Beneficial Effect of Niobium Alloying in Gray Cast Iron – Fundamentals and Applications

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## Abstract

Gray cast machinable iron consists of flake or spheroidal graphite in a ferritic, pearlitic, austenitic or martensitic matrix. This variety of microstructural combinations is used in a multitude of applications. Typical examples are vehicle brake systems, combustion engine blocks and machinery equipment.

The particular microstructural design of gray iron and thus its characteristic properties is controlled by the alloying concept and by the casting as well as heat-treating process. The standard alloying elements in gray cast iron besides of carbon are silicon and manganese. Other elements like nickel, molybdenum, vanadium and magnesium are added to influence the microstructure.

Although the research work on the effect of niobium in cast iron is rather limited, a few statements on the effect of niobium can be safely made:

- Nb additions up to 0.3% tend to improve the mechanical properties of gray iron resulting from a reduction in the cell size and correspondingly blunt graphite flake size.
- Nb decreases the tendency to produce chill carbides due to an inoculating effect and the increase in cell count.
- Nb is a mild pearlite stabilizer and refiner.
- Nb alloyed in larger amounts forms primary MC-type carbides of high hardness improving the wear resistance of cast iron.

Based on these effects specific applications of niobium-alloyed cast iron have been developed leading to appreciable technical and economical benefits. Work rolls for steel mills are often niobium-alloyed giving the advantage of reduced wear and thus longer endurance. Alloying of niobium to brake discs and drums allows to increase the graphite content at a given strength level and thus to optimize the heat conduction and damping behavior. The strength increasing effect of niobium can also be of advantage for the production of thin walled engine blocks. Additionally niobium helps to avoid the formation of chill structures which are difficult to machine.

The present paper discusses the effects of niobium in cast iron in more detail and also disseminates practicable alloying techniques in the foundry.

## Introduction

Gray cast iron is by far the most important casting material. Its worldwide production is far higher than that of all other casting alloys. It is produced over a wide range of carbon equivalent (CE) values as its strength, hardness, and other properties are related to that CE-value. Compositions with low CE-value give higher strength and hardness while high CE-values result in lower strength but better machinability, higher damping capacity and thermal conductivity. Furthermore, the casting behavior is also improved. The CE value is primarily

controlled by carbon (C) and silicon Si according to CE = C + 0.33Si and a CE-value of 4.26 represents the eutectic composition.

The usual graphite morphology in cast iron is lamellar graphite. The graphite lamellae visible in a typical micrograph are in reality interconnected to form a three-dimensional cabbage like structure. Together with the matrix occupying the space between the lamellae, a so-called eutectic grain or cell is formed. Suitable etching can make the grains visible because the grain boundaries are enriched in segregating elements like phosphorus, chromium and other carbide forming elements.

It is possible to modify the form of graphite by a treatment with magnesium and/or rare earth metals to achieve a nodular form. The resulting cast iron is called nodular or spheroidal graphite iron, or ductile iron. It has higher strength with improved ductility as compared to gray iron. Nodular cast iron and compacted graphite cast iron are usually produced with eutectic or slightly hypereutectic compositions. The CE-value has little effect on their properties. Compacted graphite iron (CGI) has properties being approximately in between those of gray and nodular iron.

A wide range of matrix structures is available: ferritic, ferritic-pearlitic, pearlitic, or austenitic, with different combinations of strength, ductility, wear resistance, etc. The eutectoid transformation not always follows the stable diagram and the ferrite transformation can be incomplete or can be often totally suppressed in favor of pearlite formation. Pearlite consists of ferrite and cementite lamellae and is formed according to the meta-stable Fe-C-diagram. The interlamellar spacing of the pearlite depends on the cooling rate and can be refined by accelerated cooling or alloy additions resulting in higher strength, hardness, and wear resistance. Higher alloy additions will promote bainitic, martensitic or even austenitic microstructures. In fact, today gray iron is mostly produced having a predominantly or even fully pearlitic matrix, exposing higher strength and wear resistance than ferrite.

**Effects of Niobium in Gray Cast Iron**

From laboratory experiments [1, 2] as well as from practical experience in a variety of applications niobium was found to have an inoculation effect and to influence the microstructure of gray cast iron (**Figures 1 and 2**).

Nucleation (inoculation) effetcs of Nb:
- Nb(C,N) has a graphite nucleating effect but less powerful as FeSi.
- High temperature or long holding times have apparently no negative effect on the nucleating potential of Nb(C,N) as compared to standard inoculants showing fading under such circumstances.
- Nb alloying enhances the degree of nucleation above that of the standard inoculants.
- Nb alloying promotes pearlite formation even at enhanced inoculation.

Microstructural effects of Nb:
- Nb alloying decreases the tendency to form chill carbides.
- Nb alloying (<0.3 wt.%) reduces the depth of clear chill and of the mottled zone.
- Nb alloying increases the number of eutectic cells and leads to shorter and finer graphite flakes.
- The interlamellar spacing of pearlite is being refined.

All these effects saturate at about 0.3 wt.% of Nb as can be seen from **Figures 1 and 2**. Foundries that have established the use of Nb already claim that the addition of up to 0.3 wt.% Nb always improves the properties of gray cast iron [3]. It is important, however, that the alloyed FeNb is fully dissolved and NbC precipitation is homogeneous.
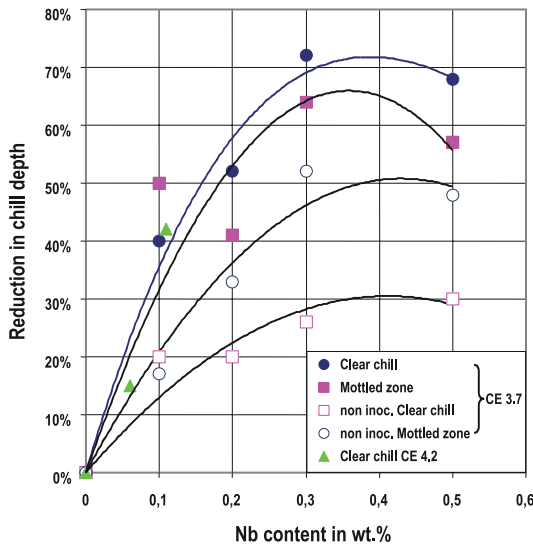


*Figure 1: Influence of niobium addition on the chilling behavior of various iron types with and without inoculant.*
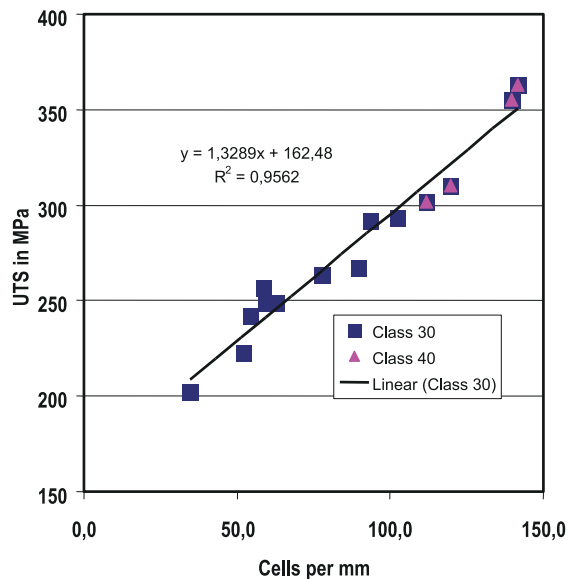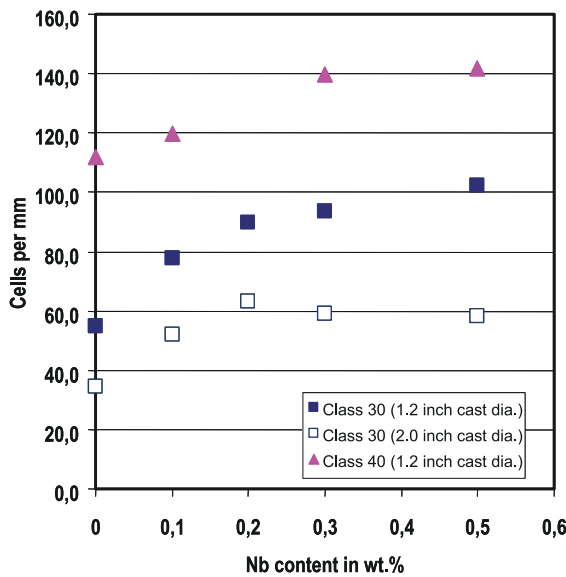


*Figure 2: Influence of niobium addition on the eutectic cell count and on the tensile strength in different types of gray cast iron.*

Lamellar Cast Iron

A large volume of coarse graphite is used for brake rotor castings to obtain a high damping capacity. Alloying elements such as chromium and molybdenum, which increase hardenability, guarantee the formation of a pearlitic microstructure, thus offering appreciable strength. In the framework of optimizing this alloy, niobium microalloying up to 0.09% Nb was investigated [4]. It was found, that the refinement of the eutectic cells by niobium microalloying is the key parameter to optimise strength and damping capacity. Besides the fact that the eutectic cell exhibited practically half the size when adding 0.09% Nb also the interlamellar spacing of the pearlite became refined, accordingly. However, in order to

maintain rather coarse graphite a hypereutectic composition such as 3.8% C – 2.5% Si – 0.7% Mn – 0.25% Cr – 0.20% Mo – 0.09% Nb is required.

The good thermal conductivity is used to reduce the formation of heat cracks especially in brake disks for trucks. Higher levels of niobium are found as niobium carbides located inside the austenite dendrites. The addition of about 0.4% Nb to 3.8% C – 2% Si – 0.7% Mn – 0.4% Cu and 0.3% Cr to pearlitic cast iron [5] increases the strength and reduces the wear during the braking operation by uniformly distributed niobium carbides. As a result, such brake disks last at least eight times longer than the brake pad linings.

Nodular Cast Iron
In case of dynamically loaded components, ductility is an important property in addition to strength. In this case, the globular form of graphite is desired as it occurs in tempered iron or especially nodular cast iron.

A Brazil made compact car uses a piston ring produced with nodular cast iron (3.6% C, 2.15% Si, 0.20% Mn, 0.55% Ni, 0.18% Mo, 0.05% Mg) containing 0.5% Nb (6). The niobium containing casting exhibited 15 to 20% less wear than the niobium free rings of the same nodular iron. It was obvious from the wear behavior, that any scratches at the surface were interrupted at niobium carbide particles. Rather than in a eutectic arrangement, niobium carbides sized up to 5 microns exist often in a rather compact form, indicating that they have been formed directly from liquid iron. The base microstructure is a tempered martensite. Thus, a high tensile strength of above 2000 MPa is achieved. It confirms earlier results obtained in China, where the alloying of niobium to piston ring material allowed the number of rings to be reduced from five to four [7].

Nodular cast iron reinforced with niobium carbide is also widely used in rolls for hot rolling as their performance is about 40% higher than that of rolls without such NbC addition [8]. It is also in agreement with another study of the effect of niobium in ferritic nodular cast iron [9] indicating that with higher niobium addition the strength increases and the toughness is impaired. The NbC particles do not influence the graphite formation, if they are equally distributed all over the matrix.

Mottled Cast Iron (Indefinite Chill)
Mottled iron is characterized by a microstructure, which contains both, cementite and graphite. A special type called indefinite-chill contains fine interdendritic graphite flakes. This type is widely used in rolls for hot rolling, where the carbide phase improves abrasion resistance while the graphite present in the working layer reduces the friction between roll and piece and minimizes thermal shocks. A typical alloy would contain about 3.3% C, 0.8% Mn, 0.9% Si, 1.8% Cr, 4.4% Ni and 0.4% Mo. The base composition is similar to Ni-Hard exposing a mainly bainitic or martensitic matrix. The graphite precipitates in this alloy are obtained by a proper balance of graphite promoting elements, such as silicon and nickel, and carbide promoting elements, such as chromium and molybdenum, and inoculation.

If about 1.5% Nb is added to such an alloy together with the stoichiometric amount of carbon, primary NbC carbides are formed further improving hardness and wear resistance without deteriorating the graphite morphology. As a result, the roll performance (tonnes of rolled steel per mm of wear due to rolling and grinding) is improved by more than 30% [8].

**Precipitation of Niobium in Cast Iron**

The equilibrium phase diagram from Fe+4.24% C – NbC is shown in **Figure 3**. It indicates that very small additions of niobium (<0.1%) have no influence on the solidification temperature and sequence. NbC will be formed during the eutectic reaction. The solubility of Nb in the austenite of cast iron alloys is very low just like that of Ti (**Figure 4**). This is in marked contrast to V having considerable solubility in austenite. It is therefore clear, that Nb does not interfere with metallurgical reactions after solidification.
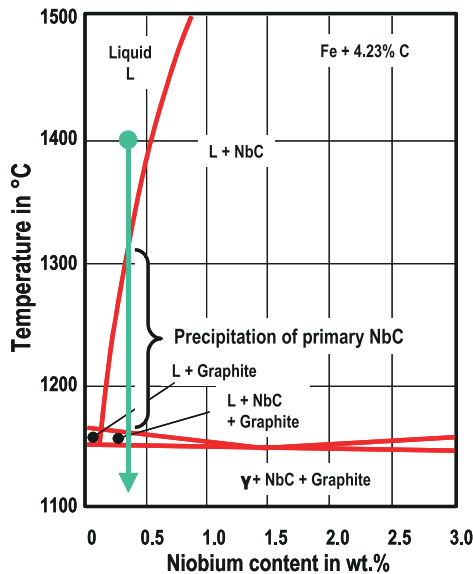


*Figure 3: The iron rich corner of the binary system Fe+4.23 %C – NbC indicating the precipitation sequence for 0.3 wt.% Nb alloying.*
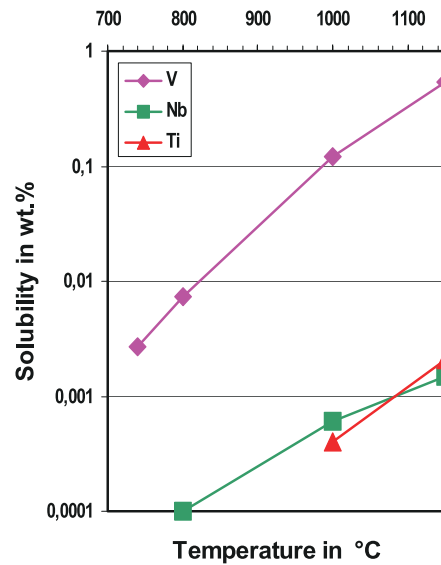


*Figure 4: Temperature dependence of refractory metals solubility in austenite containing maximum carbon (line E-S in the Fe-C phase diagram).*

However, with increasing niobium level above 0.1% primary NbC carbides will be formed in the liquid iron. These NbC precipitates could act as nuclei for the eutectic reaction, i.e., the transformation of the liquid phase into austenite and graphite (or cementite). This explains the observation, that the eutectic cells become finer with niobium additions. If the niobium content exceeds the alloying limit of 0.2%, such primary carbides are formed already at elevated temperature becoming coarser with time and can thus be found in the microstructure as NbC by optical metallography. Larger NbC particles improve the hardness and are beneficial for the wear resistance.

Primary precipitated NbC appears in different forms due to its cubic face centered structure and its typical crystal growth. It can grow to large carbides already before casting. Due to its high melting point Nb tends to segregate in the melt and local concentration can lead to dentritic structures reaching large size. Such dentritic morphology or clusters of NbC particles are detrimental to toughness. The formation and morphology of NbC can however be influenced by secondary metallurgical treatment of the melt. Desoxidation of the melt with Al forms $Al_2O_3$ nuclei having a good lattice compatibility with NbC [10]. Also the addition of a small amount of Ti has a nucleating effect. The affinity of Ti to C and N is higher than that of Nb. Thus primarily Ti(C,N) nuclei are formed on which Nb grows isomorphically to small cubes [11]. Furthermore, a relatively late addition of FeNb to the melt shortens the growth period for NbC precipitates.

**Figure 5** shows the appearance of primary NbC particles in different types of gray iron. It is obvious that the morphology of the graphite phase is not affected by the presence of the NbC particles.
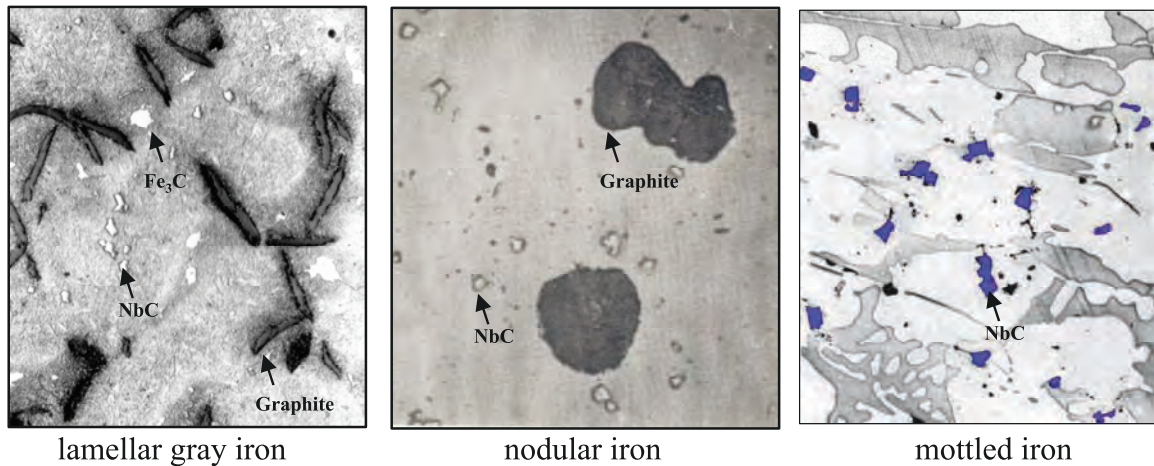


| lamellar gray iron | nodular iron | mottled iron |

*Figure 5: Microstructures of different Nb alloyed gray irons containing NbC particles.*

**Niobium Alloying Technique**

The standard Nb compound for addition to iron and steel is ferro-niobium with about 66% Nb. This composition almost corresponds to the intermetallic phase FeNb, known as the μ-phase in the Fe-Nb phase diagram [12]. Ferro-niobium has a rather high melting point with a solidus and a liquidus temperature of 1580 °C 1630 °C, respectively. Consequently, this alloy does not melt but has to be dissolved, even in steelmaking. Besides of the lower melting temperature in cast iron production as compared to steelmaking, also a different dissolution mechanism applies, slowing down this reaction as is explained by the following micrographs [13]. **Figure 6** shows an undissolved FeNb lump present in frozen cast iron. The lump is surrounded by concentric rings. The mechanism of dissolution becomes clearer at increased magnification of the interface between the ferro-niobium and the frozen melt. On the surface of the FeNb, several phases are visible exhibiting higher carbon content than the FeNb itself. Only the surface particles of a few microns in size are released to the melt.
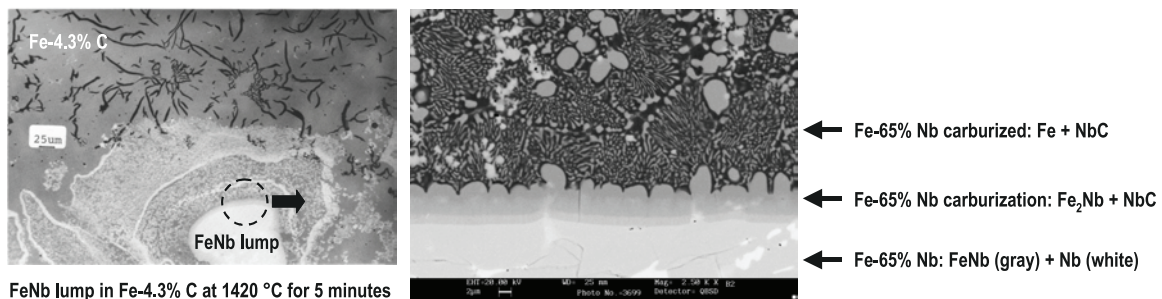


*Figure 6: Ferro-niobium lump in cast iron and magnification of the interface zone.*

The Fe-Nb-C diagram explains the nature of the different phases seen in this reaction. First the surface picks up carbon, thus, besides the μ-phase (FeNb) also the λ-phase ($Fe_2Nb$) as well as niobium carbide ($Nb_2C$) are observed. However the carburization is continuing and finally $Nb_2C$ and NbC are released to the melt. As a result of the carbon surplus, only NbC will exist in the melt that will be dissolved to an extent allowed by the equilibrium, i.e.

around 0.8% Nb at 1500 °C (see **Figure 7**). During freezing, however, the dissolved niobium will re-precipitate and form NbC particles again: the size of these particles is not related to that of the parent NbC particles that had been released to the melt during the dissolution of the ferroalloy.
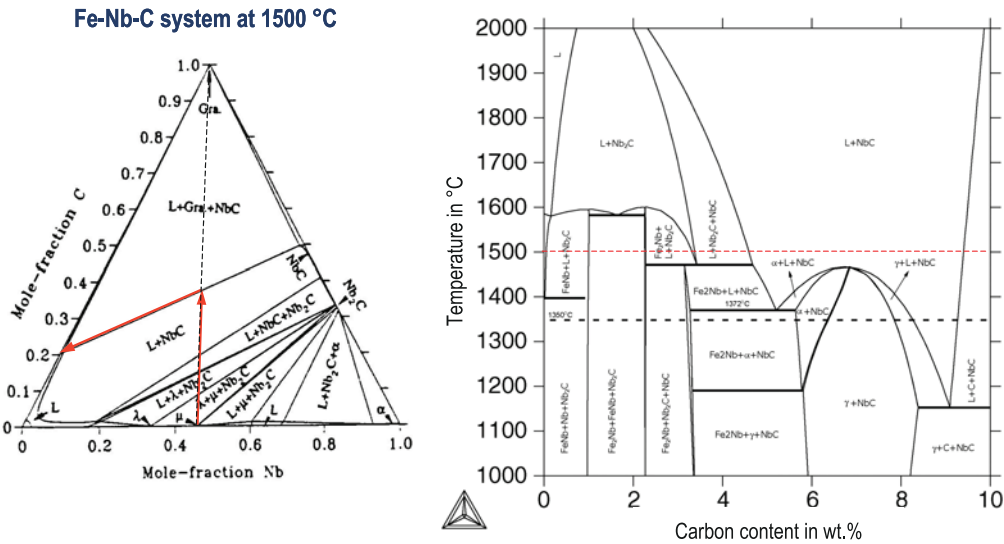


*Figure 7: Section at 1500 °C of the Fe-Nb-C system according to Huang [12] with arrows describing the carburizing and dissolution process of FeNb in cast iron.*

The different mechanism of FeNb dissolution in high carbon iron as compared to low carbon steel has an effect on the kinetics of this process. Both, the slower dissolution mode as well as the relatively low melting temperature could explain the fact that FeNb only partially dissolves. **Figure 8** shows the calculated time required for complete dissolution of a given FeNb lump diameter. Some turbulence in the molten bath, which can be obtained by stirring or injection, improves the dissolution kinetics.
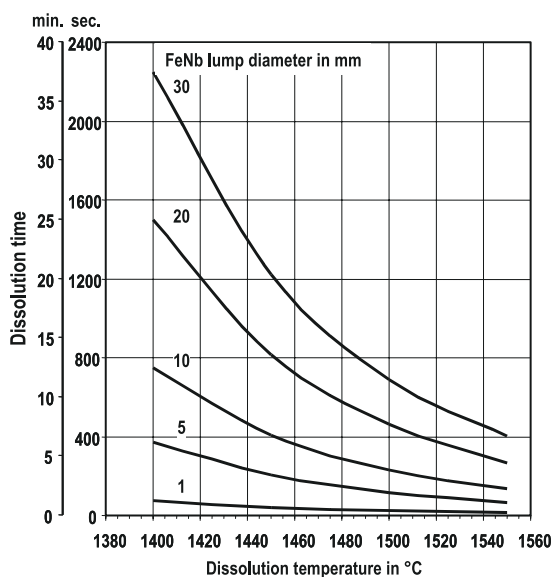


***Figure 8**: Dissolution time of FeNb in eutectic iron (4.23 %C) as a function of bath temperature and FeNb lump size.*
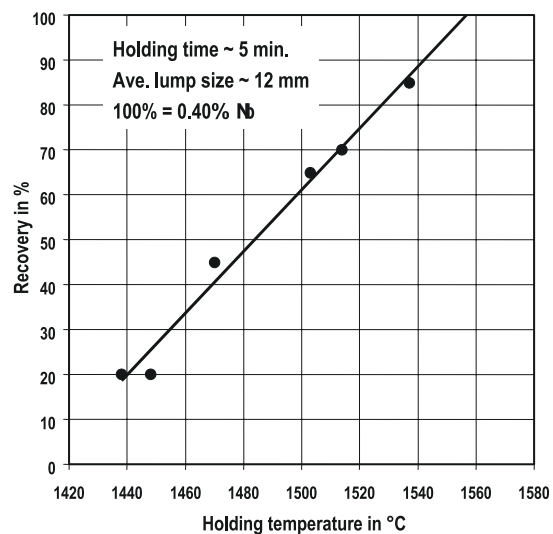
***Figure 9:** Recovery of FeNb in eutectic iron as a function of holding temperature.*

Considering however a typical melting temperature of 1400 °C in a foundry, **Figure 8** predicts a period of approximately 15 minutes for the dissolution of a FeNb lump of 12 mm (1/2 inch) diameter. Consequently, two major methods are practiced to alloy FeNb in an economic way:

- Either bulky material is charged together with solid scrap, thus allowing a long holding period in the furnace.
- Or in case, the FeNb is added just during tapping and only little time until casting remains, rather fine-grained FeNb has to be added, being dissolved within a few minutes. Accordingly, many foundries order FeNb of size 1-3 mm.
- The most effective way, however, is the injection of powdered material [14] as cored wire, since both, the fine particle size and the bath turbulence favor a reduction of dissolution time.
- Superheating the melt in a holding furnace is alternative means, to overcome poor recovery (**Figure 9**).

## Summary

Niobium is a very effective alloying element in cast iron since it forms primary carbides, exhibiting a fine particle size and homogeneous distribution, thus, resulting in improved wear resistance. Furthermore, niobium causes a refinement of the eutectic cell structure resulting in increased strength. It has to be taken care, however, that the added ferro-niobium is being dissolved in the liquid iron to a high degree before casting. This can be achieved by various alloying strategies.

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