NIOBIUM IN CAST IRON

Introduction and Definitions

The limit between wrought iron (steel) and cast iron is at about 2% carbon. Above this limit, eutectic graphite or cementite are precipitated, as can be seen in the iron-carbon two-phase diagram, Figure 1.

Iron with such high carbon content exhibits a relatively low melting point of about 1400 °C, which further decreases to 1150 °C once the eutectic point at about 4.3% carbon is reached. The low liquidus temperature facilitates the casting operation. However, as a result of the high carbon content, iron with 2 to 4% C is too brittle for hot forming by rolling or forging. Therefore, the net shaping of the material is usually achieved by casting and machining.

Figure 1: The stable and metastable iron-carbon diagram (1)

According to the colour of a fractured surface of cast iron, one distinguishes between grey and white cast iron. In grey or graphitic cast iron the carbon exists in the form of graphite. This corresponds to the stable Fe-C diagram represented by dotted lines in Figure 1. In white cast iron the carbon is forming the Fe₃C carbide cementite and the alloy has solidified according to the metastable Fe-C diagram (solid lines in Figure 1). Cast iron containing both, graphite and cementite is called mottled iron.

Carbon can precipitate either as lamellar graphite (grey cast iron), nodules or spheroids (nodular or spheroidal graphite iron, or ductile iron), or in a compact or worm-like form (compacted graphite or vermicular graphite iron). By suitable heat
treatment, the cementite of white cast iron can be transformed into a globular graphite type being typical for malleable iron.

The stable Fe-C diagram or grey cast iron is promoted by higher carbon content, slower cooling rate, or additional heat treatment. Other elements play also an important role as they can either promote graphite or cementite formation. Graphitising elements are e.g. silicon, copper, nickel, and aluminium; cementite promoters are chromium, manganese, molybdenum, vanadium, and sulphur. Elements like titanium or niobium form primary carbides and therefore have nearly no effect on the eutectic solidification. Various alloying elements can also change the carbon solubility in the melt, shift the eutectic carbon content to higher or lower concentrations and increase or decrease the liquidus as well as the eutectic temperature. In order to simplify the issue and avoid working with ternary and quaternary phase diagrams, the effects of the alloying elements are summarized in a carbon equivalent (CE):

\[
\text{CE} = \% \text{C} + 0.33\% \text{Si} + 0.33\% \text{P} + 0.074\% \text{Cu} + 0.053\% \text{Ni} - 0.027\% \text{Mn} - 0.063\% \text{Cr}
\]

A carbon equivalent of 4.26% represents iron of eutectic composition.

Grey 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 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 behaviour is also improved.

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 grey 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 grey and nodular iron.

If the solidification follows the metastable Fe-C diagram, white cast iron is obtained. Its formation will be promoted by rapid cooling or chilling (chilled iron), low silicon levels, and /or addition of chromium. White cast iron is especially
applied in mining and earth moving equipment and contains often rather high chromium contents. The good abrasive wear resistance of this material is a result of its rather high carbide content, but unfortunately this is often combined with a reduced toughness reducing the performance under impact loads. Therefore niobium carbide offers a promising alternative, since it forms hard and discontinuous MC carbides. Especially in hard facing electrodes very high niobium contents of more than 5% Nb are common. However, this application will not be further discussed in this information leaflet.

Transitions between white and grey solidification can occur as a result of differences in the cooling rate between surface and centre of a casting. Such transitions are also obtained by special alloy additions or inoculation. The structure is white with inclusions of either compact lamellar graphite eutectic cells, graphite nodules, or alignments of graphite flakes following primary dendrites which is called ‘indefinite-chill’.

A wide range of matrix structures is available: ferritic, ferritic-pearlitic, pearlitic, or austenitic, with different combinations of strength, ductility, wear resistance, etc.

Following the stable Fe-C diagram, the development of the microstructure can be explained by the example of iron containing 3% C as follows: When the temperature of about 1300 °C is reached, firstly austenite is formed from the liquid iron. While the austenite contains less carbon than the original melt, the remaining liquid becomes richer in carbon. When a temperature of 1153 °C is reached, the austenite contains 2.03% C and the liquid has 4.24% C. At this temperature the liquid phase transforms entirely according to the eutectic reaction into austenite and graphite. Besides the graphite formed during the eutectic reaction, more graphite is being precipitated from the austenite upon further cooling and – for equilibrium condition - at 738 °C the remaining austenite, which contains only 0.7% C, transforms according to the eutectoid reaction into ferrite and graphite.

However, this sequence is only a theoretical approach as it is difficult to define the various microstructural features along with their history of formation occurring in reality. For instance, Fe3C might be formed first as a result of undercooling and later on transform further into iron and graphite. Furthermore, any graphite formation prefers nucleation sites on existing graphite, thus it is very difficult to distinguish between primary, eutectic, secondary and eutectoid graphite. The graphite is becoming coarser at slower cooling rates. It has to be mentioned that primary graphite, which should be formed already in the liquid phase at carbon contents above 4.25%, rarely exists in cast iron since it will segregate towards the surface of the melt and separate.

Furthermore, the eutectoid transformation not always follows the stable diagram and the ferrite transformation can be incomplete or can be often totally suppressed in favour 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 grey iron is mostly produced having a predominantly or even fully pearlitic matrix, exposing higher strength and wear resistance than ferrite.

**Examples of Application**

**Grey Cast Iron**

The advantages of flake graphite are reflected in excellent machinability, good thermal conductivity of the lamellae and the effective absorption of mechanical vibrations and their dissipation.

The good thermal conductivity is used to reduce the formation of heat cracks in brake disks for trucks. 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 (2) 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.

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 (3). 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 (24 cells per mm$^2$) 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 was needed:

3.8% C – 2.5% Si – 0.7% Mn – 0.25% Cr – 0.20% Mo – 0.09% Nb.

These results confirm earlier findings (4) such as the refinement of eutectic cells by adding niobium as shown in Figure 2. During that study it was found that niobium additions above a level of about 0.25% do not result in further strength increase, Figure 3. Higher levels of niobium are found as niobium carbides located inside the austenite dendrites. These hard particles are effective to improve abrasive wear. Practical examples of niobium containing cast iron were also demonstrated in that paper. In addition to brake drums also the cylinder liner for a motorcycle was made from such an alloy type. Besides, an adequate phosphorus addition was used to achieve a higher fluidity of the melt.
**Figure 2:** Eutectic cells in cast iron (CE = 4.2) inoculated with 0.4% FeSi

**Figure 3:** Influence of niobium addition on the tensile strength of cast iron (0.4 % FeSi inoculation)
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 (5). Figure 4 shows the micrograph of the niobium containing casting, which exhibited 15 to 20% less wear than the niobium free rings of the same nodular iron. It was obvious from the wear behaviour, that any scratches at the surface were interrupted at niobium carbide particles. Rather than in an eutectic arrangement, the 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 (6).

![Figure 4: Not etched micrograph of a piston ring from niobium containing nodular iron](image)

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 (7). It is also in agreement with another study of the effect of niobium in ferritic nodular cast iron (8): 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% (7, 9)

**Niobium in weldable Ni-Resist**

Ni-Resist cast iron is a family of cast iron alloys with a sufficiently high nickel content to produce an austenitic structure having unique and superior properties. The nickel content of that alloy is between 20 and 35% depending on the required properties. The properties of interest include resistance against corrosion, heat and thermal fatigue, low temperature toughness, low and high thermal expansion coefficients, and low magnetic permeability. Ni-Resists are available with lamellar and nodular graphite, but today the grades with nodular graphite (ductile Ni-Resist) are of greater importance (10).

Ductile Ni-Resist alloys are all capable of being welded, provided correct welding parameters are set and magnesium and phosphorus contents are controlled to proper limits. Good weldability is especially required for large corrosion resistant castings like pump parts where small foundry defects and damage occurring in service have to be repaired. Sometimes also assembly welding is necessary to build larger units. The presence of magnesium, required for the spheroidization process, decreases the ductility at welding temperatures, thus, small cracks can occur in the weld heat affected zone. To overcome this problem, alloy Ni-Resist D-2W was developed, making use of niobium addition combined with the control of silicon, phosphorus and residual magnesium contents. Practical experience has demonstrated excellent welding results after repair of major casting or service defects. The user properties are the same as for the niobium-free Ni-Resist grades D-2 and D-2B and thus the alloy has been included in the Ni-Resist standards worldwide.

In practice, D-2W is even supplied by foundries when the equivalent Ni-Resist grades without niobium are actually specified. This is to initially avoid problems should welding become necessary. Attention must be paid not only to control the niobium content (0.12 – 0.20%), but also silicon (2.25% max.), phosphorous (0.04% max.) and magnesium (0.05% max.). An interrelationship also exists between these elements, which can be described by two formulae (11):

\[
\% \text{Nb} \leq 0.353 - 0.032(\% \text{Si} + 64 \% \text{Mg})
\]

\[
\% \text{Nb} \geq 0.0286(\% \text{Si} + 64 \% \text{Mg} - 5.6) + 8(\% \text{P} - 0.025)
\]
**Figure 5** shows these relationships as well as the range of critical alloy contents for crack free welding.

![Figure 5: Influence of various alloy elements on the tendency to form heat affected zone cracks in Ni-Resist D2 (GJSA-XNiCr20.2)](image)

A niobium addition seems to have a beneficial effect also on other than Type D-2W Ni-Resist alloys, although research in this area has not been extensive. Typical compositions are summarised in **Table 1**.

**Table 1.** Chemical composition recommended for crack free welds of Ni-Resist D-2 with low and high phosphorus content (11)

<table>
<thead>
<tr>
<th>Element</th>
<th>Low phosphorus</th>
<th>High phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total C</td>
<td>2.5 – 3.0</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>1.5 – 2.2</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>1.0 – 2.5</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>2.0 – 2.5</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>19 – 22</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>≤ 0.08</td>
<td>≤ 0.05</td>
</tr>
<tr>
<td>P</td>
<td>≤ 0.025</td>
<td>≤ 0.04</td>
</tr>
<tr>
<td>Nb</td>
<td>0.06 – 0.11</td>
<td>0.12 – 0.17</td>
</tr>
</tbody>
</table>

**The Role of Niobium in Cast Iron**

The equilibrium phase diagram from Fe+4.24% C - NbC is shown in **Figure 6**. 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.
However, a slightly increased niobium level in the range of 0.1 to 0.2% causes that 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 microalloying limit (>0.2% Nb), such primary carbides are formed already at elevated temperature. They become coarser and can be found in the microstructure as NbC by optical metallography, thus improving the wear resistance as well as hardness and strength.

It has also been found, that the microalloy addition of niobium reduces the chilling depth, thus promoting the formation of grey cast iron (12). A satisfactory explanation, however, could not be given.

**Niobium Alloying Technique**

The standard Nb compound for addition to iron and steel is ferroniobium with about 66% Nb. This composition almost corresponds to the intermetallic phase FeNb, known as the µ-phase in the Fe-Nb phase diagram (13). Ferroniobium 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 (14):

**Figure 7** 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 ferroniobium and the frozen melt, **Figure 8**. On the surface of the ferroniobium, several phases are visible exhibiting higher carbon content than the ferroniobium itself. Only the surface particles of a few microns in size are released to the melt.

![Figure 7: Ferroniobium lump in cast iron](image)

![Figure 8: Interphase of Ferroniobium and cast iron](image)

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 $\lambda$-phase ($\text{Fe}_2\text{Nb}$) as well as niobium carbide ($\text{Nb}_2\text{C}$) are observed. However the carburisation is continuing and finally $\text{Nb}_2\text{C}$ and $\text{NbC}$ 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 6**). 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 9** describes this process by means of the Fe-Nb-C system.

![Figure 9: Section at 1500 °C of the Fe-Nb-C system according to Huang (13) with arrows describing the carburising and dissolution process of ferroniobium in cast iron](image)

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, as described in **Figure 10**. The data from this diagram derive from two sources, i.e. the results for dynamic dissolution speed in cast iron were produced by (15) while the results for the static condition and the steel data came from (16). Both, the slower dissolution mode as well as the relatively low melting temperature could explain the fact that ferroniobium only partially dissolves. **Figure 11** shows the time required for complete dissolution of a ferroniobium lump of a certain diameter calculated according to the equation given by (15), representing the dynamic condition.
It was already obvious from Figure 10 that some turbulence in the molten bath, which can be obtained by stirring or injection, improves the dissolution kinetics. These calculated results are totally in agreement with data obtained by own investigations as well as results published earlier (12).
Considering however a typical melting temperature of 1400 °C in a foundry, Figure 11 predicts a period of more than 60 minutes for the dissolution of a ferroniobium lump of 30 mm diameter. Consequently, two major methods are practised to alloy ferroniobium 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 ferroniobium is added just during tapping and only little time until casting remains, rather fine-grained ferroniobium has to be added, being dissolved within a few minutes.

The most effective way, however, is the injection of powdered material (17), since both, the fine particle size and the bath turbulence favour a reduction of dissolution time. There are also several other means, to overcome poor recovery.

**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 cells giving higher strength and, thus, allowing weight reduction. It has to be taken care, however, that the added ferroniobium is being dissolved in the liquid iron. This can be achieved by a suitable alloying technique.

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