

# **NIOBIUM IN CAST IRON**

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## **Abstract**

The use of niobium in cast iron is a relatively new technology at least compared to the use of niobium in steels. The previous International Symposium on Niobium in 1981 did not cover this topic at all. Recently though some important applications for the use of niobium in various cast irons have been developed and some of these will be discussed in this paper. The use of niobium in some different rolling mill roll materials will be described in detail since this has proved to be a very successful application. The method of producing Indefinite Chill rolls containing niobium is patented by Åkers Sweden AB on a worldwide basis.

## Introduction

The use of niobium in steels has a long tradition but is in most cases restricted to micro-alloying (<0.1 %). When it comes to cast irons, as will be discussed later, the use of niobium is better described as macro-alloying (up to several percent).

The use of niobium in cast irons is still a relatively new technology as was already mentioned. A search made on the METADEX system gave for the search profile “Niobium and Cast(w)Iron” less than 100 hits, and most of them were not relevant.

Some of the most significant applications so far have been for the automotive industry such as cylinder heads, piston rings and truck brakes (1).

The ability for niobium (as for most elements in the groups 4 and 6) to form a hard, discrete and stable carbide (NbC) is very important for many wear resistant applications. In many of these applications some sort of cast iron, white, grey, nodular or malleable is used.

The aim of this paper is not to try to give a complete review of the use of niobium in all different cast irons. The main focus will be on some wear resistant applications such as rolls for hot rolling of steel and non-ferrous alloys where the use of niobium has been very successful.

### General Features when Niobium is Added to Cast Iron

Some early works (2-6) describe various aspects of small additions of niobium (<0.5%) to cast irons. These have found minor changes to the austenite stability, micro-hardness, refining of graphite structure, very small precipitations of Nb(C,N) and so on. Some of these investigations were misinterpreted or misunderstood possibly due to lack of advanced measuring techniques such as high-resolution microscopes as well as an incomplete understanding of the basic thermodynamics. As an example of this in a recent investigation (7) the influence on mechanical properties of niobium additions to a grey iron melt was studied. The result was interpreted as follows: “The effect of niobium on mechanical properties and strengthening mechanism of grey cast iron were studied. The experimental result shows that niobium obviously improves the mechanical properties of grey cast iron.” In Table I and in figures 1-2 the numerical results are shown.

Table I Chemical composition and mechanical properties of Nb cast iron  
\*CE=C%+1/3(Si+P)%

Melt	Alloy content %						CE* %	S <sub>C</sub>	Mechanical properties		
	C	Si	Mn	P	S	Nb			σ <sub>b</sub> (MPa)	HB	A <sub>k</sub> /(J·cm <sup>-2</sup> )
1	3.43	2.13	0.89	0.09	0.045	0	4.17	0.96	203.4	199	3.8
2	3.47	2.10	1.06	0.12	0.037	0.077	4.22	0.98	220.4	204	---
3	3.54	2.05	0.79	0.12	0.041	0.26	4.26	0.99	230.6	207	4.1
4	3.50	2.15	0.91	0.11	0.043	0.37	4.25	0.99	251.3	226	4.2
5	3.44	2.55	0.98	0.10	0.044	0.58	4.32	1.00	254.5	234	4.0
6	3.40	2.50	0.94	0.09	0.044	0.77	4.26	0.99	267.4	227	4.1
7	3.40	2.53	0.98	0.09	0.039	0.87	4.27	0.99	260.8	228	4.0

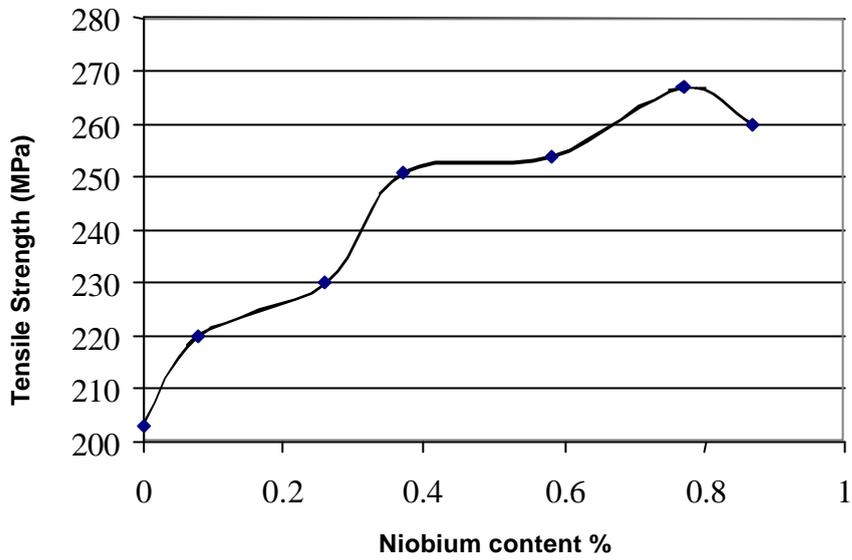


Figure 1: Tensile strength (MPa) as a function of niobium content.

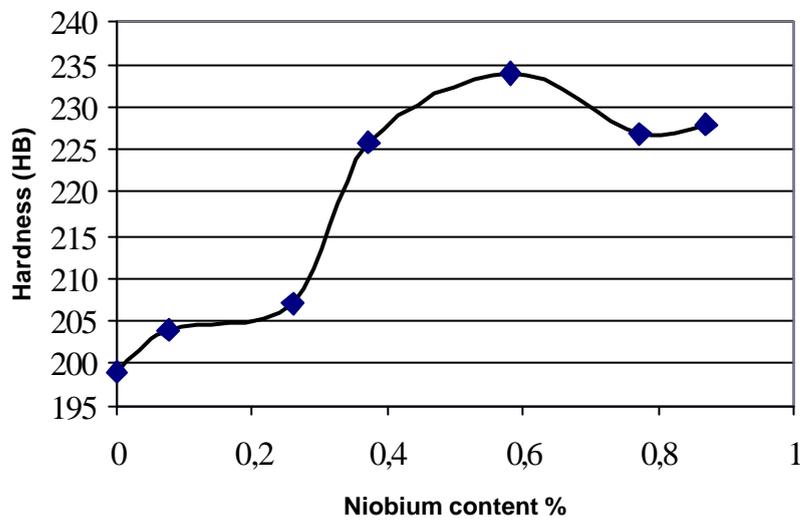


Figure 2: Hardness (HB) as a function of niobium content.

If on the other hand the hardness values are plotted as a function of the tensile strength values almost a straight line is achieved, see figure 3.

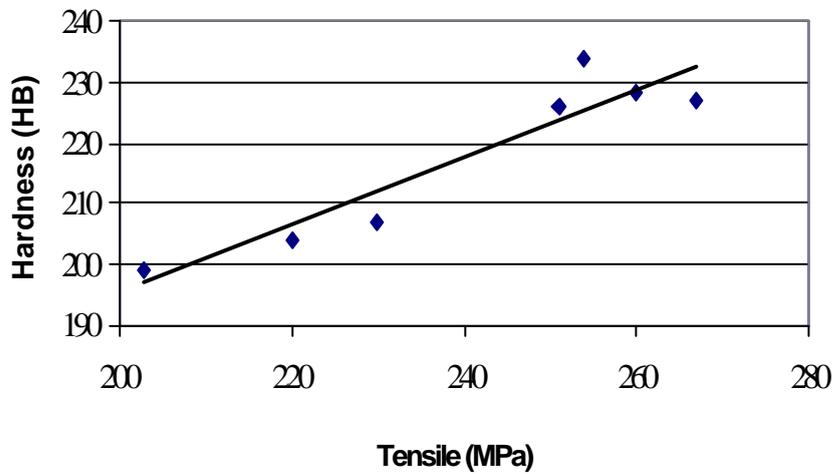


Figure 3: Hardness versus tensile strength

This might suggest that in order to study one parameter all other parameters have to be constant. If for example the hardness increase discovered in this study could be explained by the fact that niobium consumes carbon prior to the actual solidification that in turn could lead to less graphite and maybe some more carbide. The conclusion in the investigation is obviously correct but the mechanism is not fully understood or explained. The same result might have been obtained if the carbon-content of the base cast iron melt was lowered in proportion to the niobium addition.

The main focus for many of the earlier research investigations appears to be in parallel with the use of niobium in steel. That is, studying only small additions of niobium and its influence on austenite stability, grain refinement, mechanical properties and similar.

Nevertheless, it is impressive to note that a lot of work has been done in the field of cast iron 40 years ago but has not yet been strongly implemented in today's production of wear resistant cast irons. To some extent this is probably explained by the fact that the consumption of niobium is much higher in the steel sector and this sector has always been more research intensive (8-24).

If however a high enough amount of niobium (or a ferro-niobium product) is added to a high carbon melt, such as a cast iron, NbC particles will form at relatively high temperatures. These particles have several properties that are important both for the production and final use of these alloys.

Some of these important properties of NbC are shown in Table II.

Table II Some physical properties of NbC (35)

PHYSICAL PROPERTIES	VALUES	COMMENTS	US / Other Units
Density, g/cc	7.6	7.82 g/cm <sup>3</sup> theoretical	7.6 g/cc
Hardness, Rockwell A	90	At room temperature	90
Vickers Microhardness	2400		2400
Crystal Structure	Cubic	NaCl Structure	Cubic
Liquidus, °C	3575		6,467 °F

Thus as can be seen in Table II, the NbC particles have:

- A density very close to molten Iron
- A very high hardness (also in hot condition)

Furthermore:

- NbC normally forms discrete particles that are precipitated in the liquid iron and thus separated and not incorporated in the eutectic solidification.
- Niobium has a very low solubility in the austenite
- Niobium does not influence or upset the carbide/graphite distribution in Cast Iron to any significant level.

All this mentioned above offers an element which (unlike for example chromium, titanium, zirconium and tantalum) is very suitable to add almost as an "inert" element to cast iron. Most of the carbides of other elements have some very different properties from niobium such as density, influence on carbide/graphite distribution, solubility in the austenite.

## Niobium in Nodular Cast Irons

As already mentioned when niobium (or ferro-niobium) is added to a high carbon melt precipitation of NbC particles takes place at a much higher temperature than the nominal liquidus temperature for the base alloy. This is almost like a very rapid dissolution of ferro-niobium and has been described in various papers (25-32). This dissolution process has to be controlled in order not to cause agglomerations and loss of NbC to the furnace and ladle slag that reduce the recovery of niobium.

Nodular irons that are used for rolls in hot rolling and in other wear resistant applications are generally of a mottled iron type, which means they contain both graphite and carbide ( $\text{Fe}_3\text{C}$ ). This is to ensure a good enough wear resistance. Normally there are two strategies to improve wear performance:

1. Increase the overall hardness by increasing the proportion of cementite → more crack sensitive material!
2. Increase the total amount of carbides → risk to offset the balance graphite/carbide!

Other important properties are low adhesion (normally protected by surface oxidation) and good thermal crack (shock) resistance. Thermal crack resistance (TCR) which is a kind of thermal fatigue process is a function of several parameters and could be described as:

$$TCR \approx \frac{\sigma * l}{\alpha * E} \quad (1)$$

where:  $\alpha$  = thermal expansion coefficient  $\sigma$  = tensile strength  
 $\lambda$  = thermal conductivity  $E$  = Young's Modulus

It is therefore obvious that any chemical changes made to a system dedicated for rolls should not greatly influence any of the properties mentioned above. An example of a microstructure in a nodular iron grade used for hot rolling applications is shown in figure 4 below.

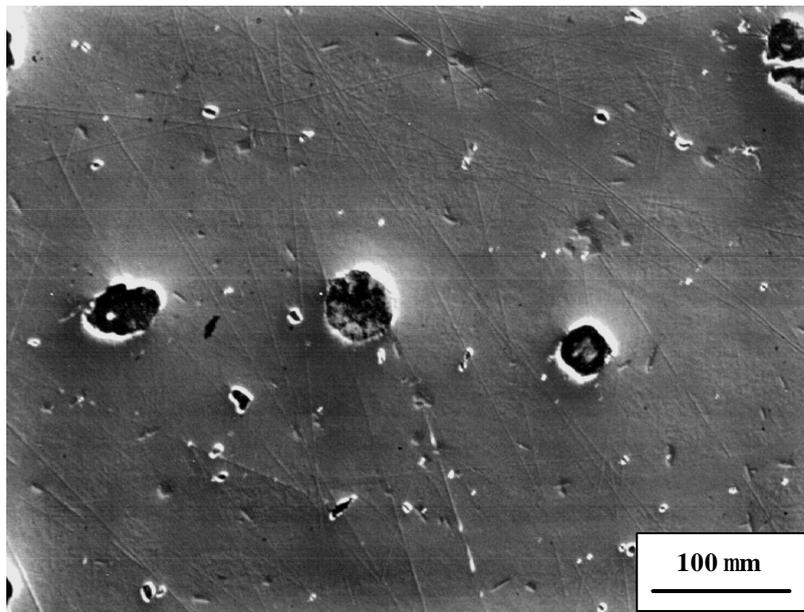


Figure 4: Nodular iron roll material with additions of niobium showing small discrete NbC particles homogeneously distributed in the structure.

A special charging and melting as well as casting procedure is necessary to ensure a good distribution of NbC particles throughout the structure. This patented technique has been used by the Åkers Group for several years with good results in the mills. Some production figures and deliveries of static nodular iron rolls (NICRA = Nodular Iron Carbide Reinforced Akers) are shown in Table III below.

Table III NICRA production and deliveries per year

Year	Cast	Delivered	Claims
1995	2	0	0
1996	2	2	0
1997	33	22	0
1998	53	49	4
1999	167	93	0
2000	196	237	0
2001	114	82	6
<b>Total</b>	<b>567</b>	<b>485</b>	<b>10</b>

Some performance results from NICRA rolls are displayed in Table IV below in comparison with standard nodular iron rolls with the same overall hardness.

Table IV Examples of performance result for NICRA rolls in various mills

Mill	Performance increase %
A	100
B	40
C	50
D	30
E	20
F	35
G	10

As can be seen the performance increase varies considerably, which is normal for small section mills where mill conditions and roll performance records are of various qualities.

### Niobium in White Cast Irons

A lot of studies have been undertaken in the field of white cast irons with niobium (33-45) especially concerning the wear properties e.g. Loper *et al.* (32) Peev *et al.* (43) and others.

Some results may be summarised as follows:

- increasing niobium content gives better wear resistance but some investigations show a minimum in wear performance in some cases without giving an adequate explanation.
- solubility of NbC in the matrix is very low
- if not highly alloyed with other elements niobium can help to increase the matrix properties.

Ogi *et al.* (37) and Matsubara *et al.* (38) have published some excellent papers describing the solidification patterns in Fe-C-Cr-Nb multi-component systems. These papers among other

things describe some interesting strategies related to inoculation with titanium in order to control the NbC morphology.

In one paper (33) the use of niobium as a substitute for molybdenum in white cast iron alloys is evaluated. The analysis is performed in terms of structural and mechanical behaviour, compared with some commercial cast grinding bodies. Thus, 10%, 15% and 20% chromium alloys were sand-cast and both structurally (component identification, distribution and morphology) and mechanically (micro-hardness, hardness and abrasion resistance) characterised. It was found that there are significant modifications in the microstructure of the alloys with the use of niobium and boron-niobium.

One of the most important results shows that a 0.5% addition of niobium instead of a 1.5% addition of molybdenum gives rise to similar wear resistance, indicating that this substitution is technically viable.

At Åkers we have for many years used niobium among other elements as an additional carbide-forming element in our high chromium iron roll material (**CICRA** Chromium Iron Carbide Reinforced Akers). This gives an additional amount of carbides, which corresponds to the actual amount of niobium addition. That is to say if 4% niobium is added the total carbide ( $M_7C_3 + MC$ ) is increased by about 4%. These kinds of rolls are normally produced by spin casting (centrifugal casting) techniques and therefore the density of early precipitates is critical.

### **Problems Specific to Centrifugal Casting**

In the centrifugal casting process one of the limiting factors is the influence of a high centrifugal force severely restraining the selection of alloying elements. The density difference between the liquid and the precipitate particle leads to a movement of the particle outward (if denser than the liquid). The speed of this movement ( $V$ ) can be very high.

According to Stokes' law:

$$V = \frac{2gr^2\Delta\rho}{9\eta} \quad (2)$$

Where  $r$  = particle radius  
 $\Delta\rho$  = density differences between particle and surrounding media  
 $\eta$  = dynamic viscosity

In spin casting the normal centrifugal force is about 150g. Equation (2) thus suggests that any movement of a particle would be 150 times faster than separation under gravity in a static system. Thus depending on the actual density of the precipitate this movement will be either to the outer portion or the inner portion of the shell material during centrifugal casting. This process is known as macro segregation or sedimentation and is in most cases related to density differences. A schematic view of this is shown in figure 5 showing the dendritic solidification pattern in combination with some precipitated cubic particles.

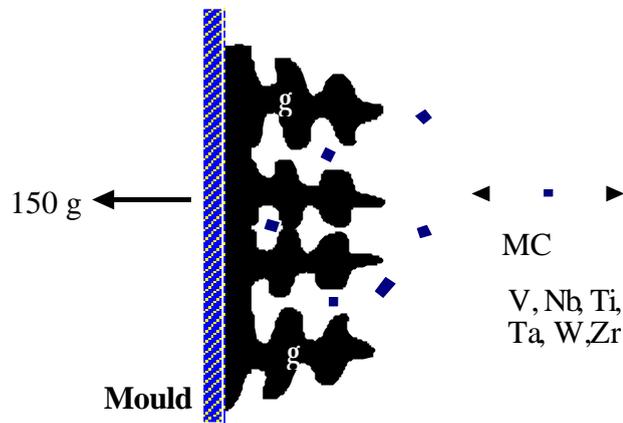


Figure 5: Schematic illustration of the solidification in a spin casting mould.

### Strategy to Counteract Problems Related to Centrifugal Casting

The problem described in the above related to centrifugal casting and precipitation of solid particles in a liquid, with a different density, could be lessened by the following proposed strategies:

1. Change the density of the liquid towards that of the particle by alloying.
2. Change the density of the particle by alloying with other carbide formers to form mixed carbide.
3. Control the precipitation temperatures of the particles by alloy design to minimise segregation (time for separation).

Initially we have chosen at Åkers to use the strategy No. 3 that is to control the temperature at which the particles precipitate and consequently avoid as much as possible any macro segregation. This could mean that particles having a density close to the melt itself are allowed to form at relatively high temperatures while particles that are much heavier or lighter than the melt have to be formed at much lower temperatures. Thus, there has to be a balance between formation temperatures and densities of the individual compounds.

### Production and Deliveries for CICRA Rolls

The production and delivery figures including claims can be seen in table V below.

Table V Production and deliveries of CICRA rolls

Year	Cast	Delivered	Claims
1998	4	4	0
1999	16	8	0
2000	25	32	0
2001	42	26	1
Total	87	70	1

A more detailed description of the various deliveries is shown in Table VI.

Performance results vary from 10-30% increase in wear resistance measured as tonnes/mm (tons of rolled product per consumed mm of roll material) depending on mill conditions.

Table VI Deliveries of CICRA rolls

Customer	No. of rolls	Dimension (mm)
CSC	14	775x1730
DLL	2	714x1880
Hoogovens	14	759x2235
Llanwern	6	750x2027
Port Talbot	2	714x2537
Sahaviriya	4	705x1725
Sidmar	14	746x2040
Sidmar	10	746x2536
Yieh Loong	4	730x2030
<b>Total no. of rolls</b>	<b>70</b>	

### Niobium in Mottled Cast Irons

A grey iron containing high enough niobium-content should be regarded as a Mottled Iron. A mottled iron is an iron containing both carbides and graphite. Normally of course and also when this definition was originated the carbide phase referred to was  $Fe_3C$  or cementite. In the case of rolling mill material the genuine mottled material is IC which stands for Indefinite Chill. The name originates from the fact that this material does not have a defined "chill depth" when submitted to a chill test. This material is an alloyed grey iron with the following nominal analysis, see table VII.

Table VII Nominal analysis of IC roll material

%C	%Si	%Mn	%Cr	%Ni
3.5	0.8	0.8	2.0	4.5

The enhanced productivity of many modern mills and increased quality requirements on rolled product has resulted in an increased demand on the roll materials. The introduction of High Speed Steel (HSS) rolls in the early stands of the Hot Strip Mill gave an important performance increase which gave rise to a need for an improvement of IC roll used in the later stands.

In the early 90's the development of carbide reinforced IC material started within the ÅKERS group (46-47). The purpose was to develop a more wear resistant IC material by adding carbide formers without losing the favourable properties of the IC material. This development is now protected by a world wide patent application. The brand name for this development is MICRA (Modified Indefinite Chill Roll Akers).

The next section will summarise the development of carbide reinforced rolls within the ÅKERS group and give examples of increased performance in different mills.

# **Niobium Carbide Reinforced IC Roll MICRA Made by Åkers**

## Introduction

The target of this development was to improve primarily the wear resistance of the IC material in order to better meet the performance of the HSS rolls that are slowly replacing the Cr rolls in the earlier stands. This should be done without upsetting the balance of carbide/graphite or to any major extent change the matrix composition of the base alloy.

## Aim - Application

The first target for the project was the Hot Strip Mill but later development work and field trials showed that there was also potential for other applications. This is discussed in other section of this paper.

## Aim - Usability and Safety

The aim was to develop a roll that in contrast to the HSS roll was easier to use for the mill and with no additional risks involved.

## Aim – Performance

Based on some early results the goal for the project was set to an improvement of on average 30% measured as tonnes/mm.

## Background – Metallurgy

In the 1930s it was discovered that the introduction of finely dispersed graphite into the white iron substantially reduced roll breakage despite providing a softer outer shell.

The presence of graphite in the working layer greatly improves the ability of the roll to withstand the thermal shocks associated with hot rolling. Graphite also reduces the friction between the roll and the strip thereby reducing the applied stress on the strip and greatly reduces the potential for welding of the strip to the roll.

Considerable efforts have been made world-wide to develop rolls that do not weld to the strip being rolled and having a better abrasion resistance than the indefinite chill rolls.

Increasing the proportion of carbides generally produces a reduction in the amount of graphite in the alloy. Numerous attempts have been made to develop alloys containing combinations of strong carbide forming elements, such as are used in Tool Steel and High Speed Steels, to replace the indefinite chill roll compositions. However, these high carbide, low graphite alloy rolls have also proven to be unsuitable for chill roll applications, because of the tendency to weld to the material being rolled and to initiate pressure cracks, much like the white cast iron chill rolls. For lack of better alternative, indefinite chill rolls have been retained in the late finishing stands of many of the modern hot strip mills. The use of strong carbide forming elements has been limited to relatively small additions, usually of molybdenum, to alter the matrix structure or extremely small additions of magnesium to control the form of the graphite.

An essential feature of the indefinite chill rolls is the balance between the alloying elements such as carbon, nitrogen and silicon which promote the formation of graphite and carbide forming elements such as chromium.

The formation of an alloy containing the proper balance of graphite and carbides requires extremely careful selection of melting stock, closely controlled melting conditions, rigid control of composition and inoculation techniques to obtain the required type and distribution of graphite. This relationship has inhibited the use of stronger carbide forming elements, which greatly skew the graphite/carbide balance in favour of carbide formation. Thus, for over four decades the use of strong carbide forming elements has been inhibited by the overwhelming need to maintain free graphite in the chilled structure of this type of roll.

Another important characteristic is the solubility of various carbide forming elements in the austenite. Some of the carbide forming elements do have a high solubility and thus influence the properties of the matrix.

A very useful tool for alloy design is Thermo-Calc® which is a computer program for thermodynamic calculations. By means of this program “phase diagrams” can be calculated and liquidus and solidus temperatures can be evaluated. Figure 6 shows an example for a calculation of an IC chill base alloy with addition of element X.

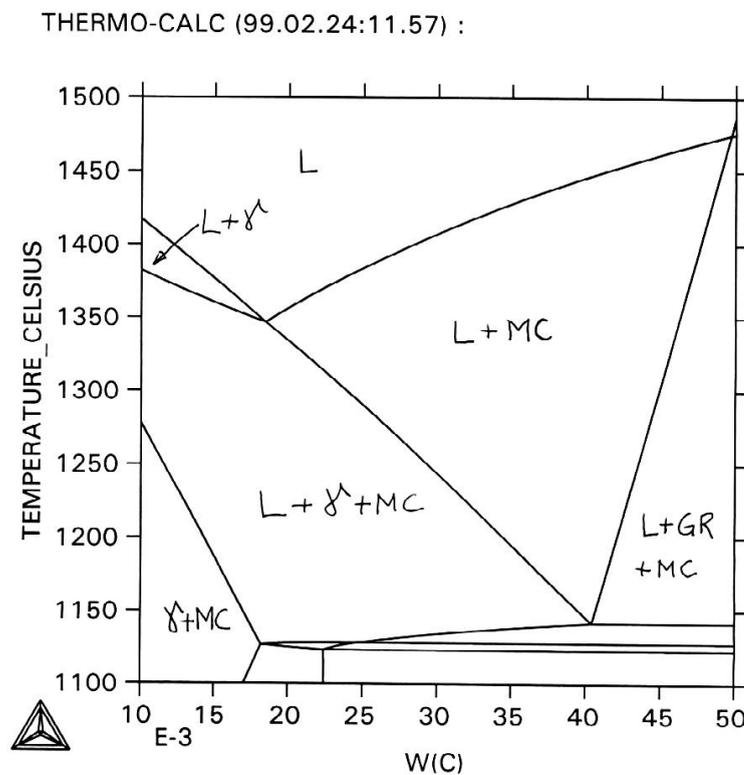


Figure 6: Phase diagram calculated with Thermo-Calc®.

As can be seen in the figure the actual liquidus temperature can be postulated for element X as a function of the C-content that is much higher than for the “actual” base alloy. By combining certain alloying elements it is possible to study the formation of complex carbides and their precipitation temperatures.

### Microstructures

Examples of the microstructure of carbide reinforced IC chill materials are shown in figure 7. The structures consists of the normal constituents graphite, cementite and a martensitic/bainitic matrix plus additional carbides. The two figures below show two different “grades” of MICRA.

The morphology of the graphite has been changed in MICRA compared with normal IC material. It is a more nodular type of graphite. In figure 8 the differences in graphite morphology are shown. This combination of specific carbide formers and a change in graphite structure leads to less wear, without changing either the mechanical properties or the fire crack resistance.

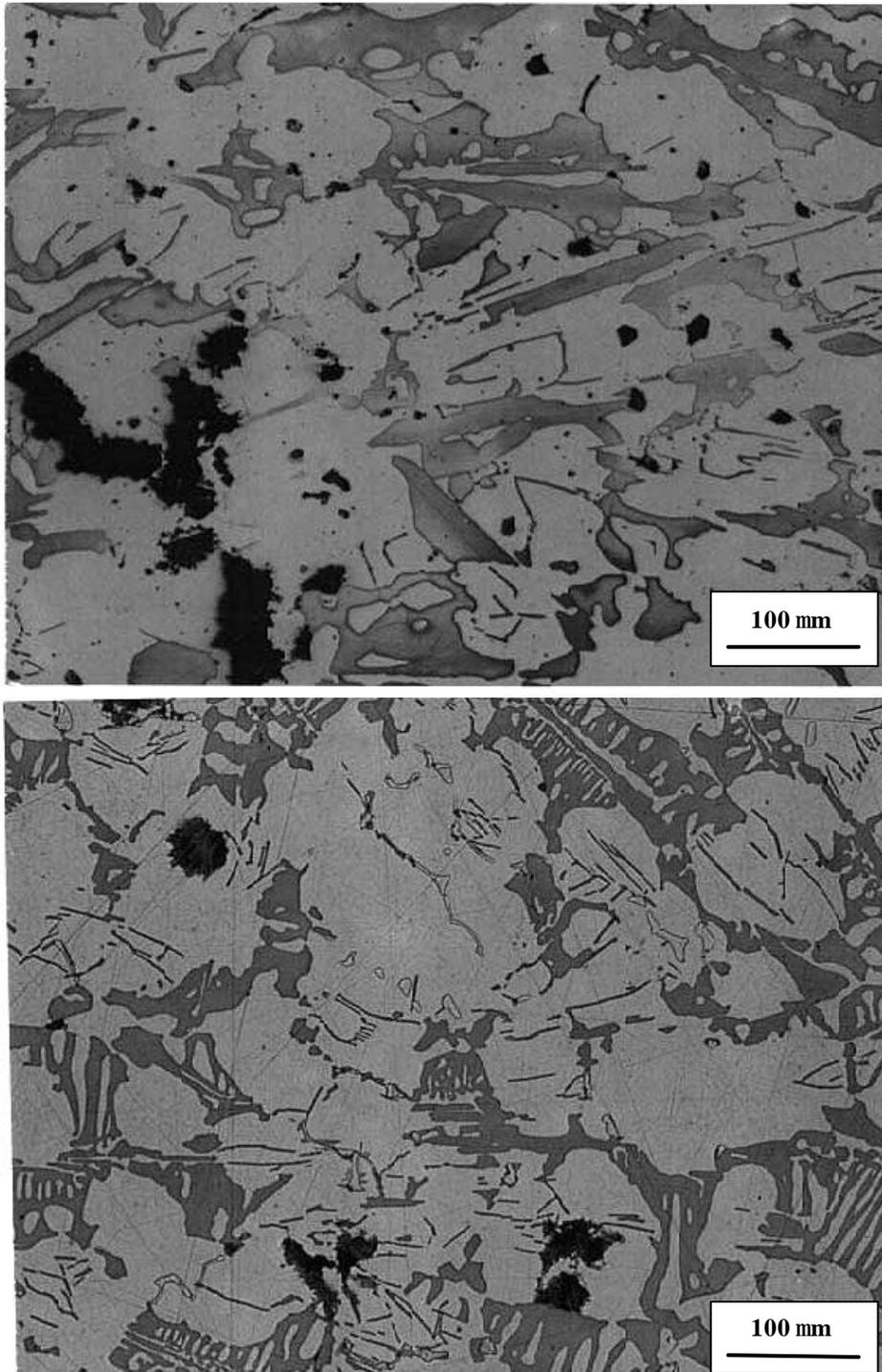
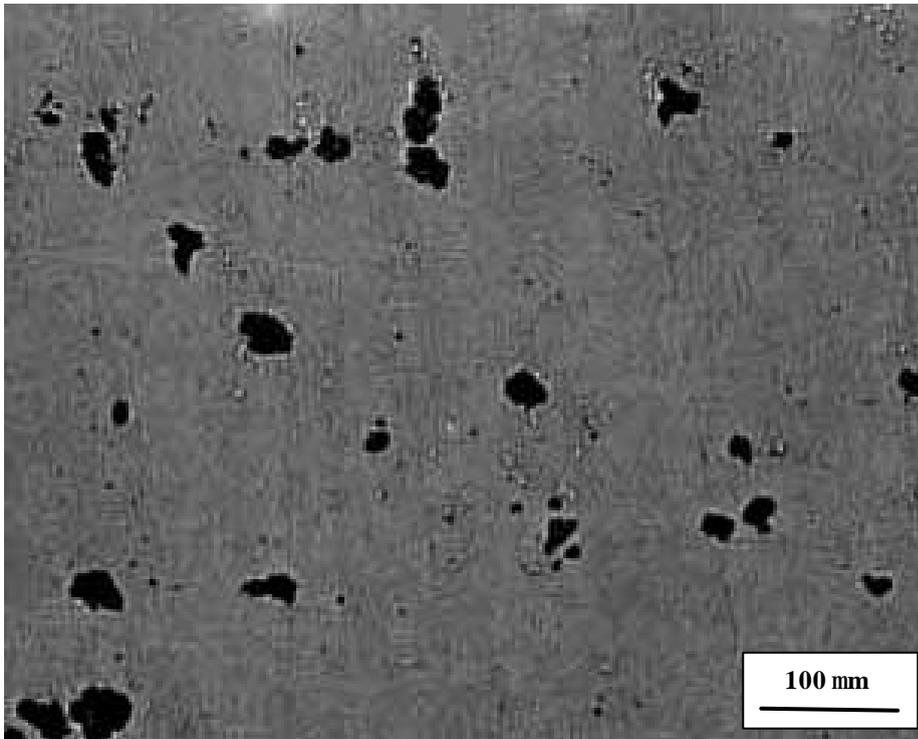
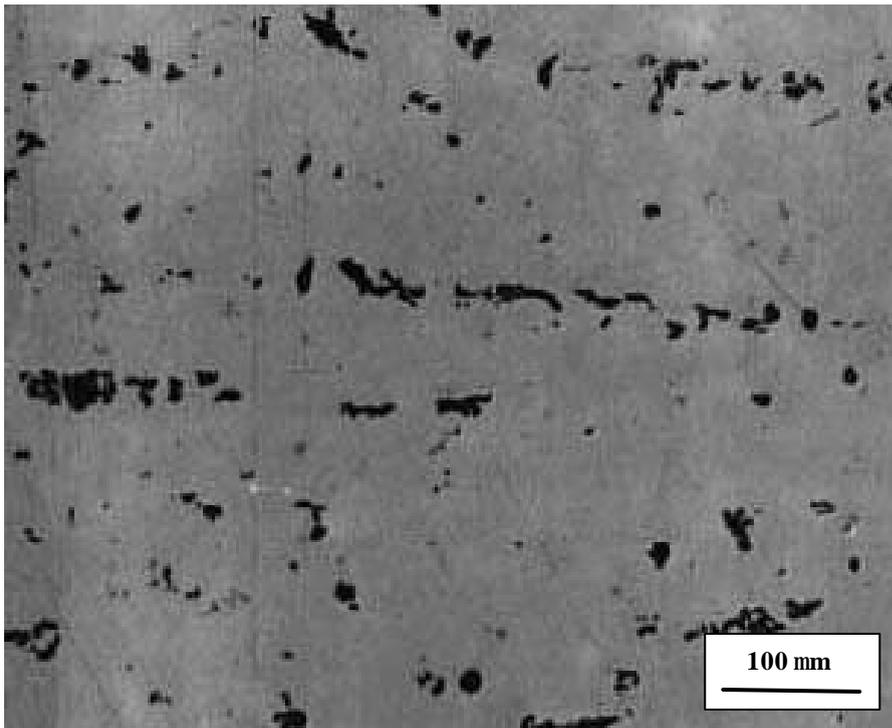


Figure 7: Some example of microstructure of carbide reinforced IC material.



*MICRA*



*NORMAL*

Figure 8. The graphite morphology of carbide reinforced and normal IC material.

#### Production and Deliveries of MICRA (Modified IC Roll Akers)

The production of these rolls has required changes and adjustments of the manufacturing steps. Some examples are:

1. Charging and melting procedure for complete dissolution of carbide-forming additions and to avoid clustering of early precipitates already in the furnace.
2. Slag removal procedure to avoid contamination of early precipitates.
3. Casting procedure to avoid clogging of casting nozzles and uneven distributions of precipitates due to uneven metal flow patterns.
4. Heat treatment sequences in order to facilitate the machining.
5. Machining procedures for optimum cutting performance.

Since 1995 more than 1900 rolls and the figures from the Åkers factory in Sweden are shown in Table X.

Table X Deliveries of MICRA rolls

Year	Cast	Delivered	Claims
1995	16	4	0
1996	34	38	0
1997	82	63	7
1998	147	119	4
1999	333	296	11
2000	397	388	8
2001	334	287	9
Total	1343	1195	39

#### Performance on Conventional and Steckel Mill

During the course of this development we have supplied as already shown almost 1900 rolls to various mills including Steckel Mill work rolls. Some of the results from these trials are shown Table XI.

Table XI Results with MICRA rolls in conventional HSM & Steckel Mill

Conv. HSM & Steckel mill	Performance increase (%)	Conv. HSM & Steckel mill	Performance increase (%)
A	22	E	42
B	30	F	35
C	35	G	25
D	55	H	37

As shown in Table XI the results in general are quite good and in some cases the improvement is over 50%. The most attractive factor with this new roll grade is that it does not need any special operational conditions in order to perform well. This is in big contrast with the use of HSS rolls that do normally need special conditions.

The improvement in performance is attributed to the fact that these rolls need less redressing than conventional IC rolls. In some cases there were some initial problems related to the fact that some mills use a standard redressing and this procedure had to be changed. Another characteristic reported from various mills is the opinion that the MICRA rolls seem to be less sensitive to damages in relation to mill stalls and similar incidents.

In contrast to conventional mills the benefit of using MICRA in Steckel mills is the possibility of prolonging the length of the campaigns. The wear resistance of the MICRA rolls seems for

some reason to be extremely good in Steckel mills. An example from a Steckel mill is shown in figure 9 in comparison with normal IC from 2 different sources.

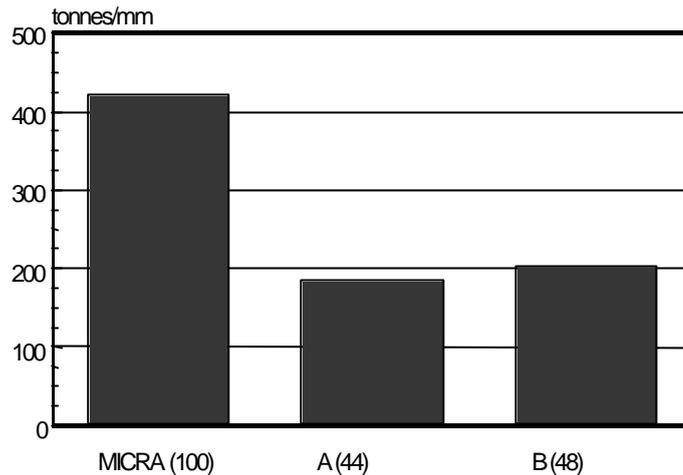


Figure 9: Performance of MICRA rolls in a Steckel mill.

### Performance of MICRA Rolls in Plate Mills

MICRA rolls used in plate mills show some good results. The results indicate performance improvement of at least 20% measured as tonnes/mm or as wear km/mm.

### **Summary**

MICRA rolls make up 50% of the total production of IC rolls at Åkers Sweden.

The earlier statements regarding improvement in performances and resistance against Mill incidents are still valid.

Generation 2 MICRA rolls are under development and are being tested in some mills.

### **Conclusions**

The purpose of this paper was to review on the use of niobium in cast irons. It was impossible to make a complete coverage of this topic even though the field is not as big as for niobium in steel. Initially investigations for the use of niobium in cast irons were focused on all the properties (creep, welding, corrosion) in a similar way to steels. Recent publications seem to be more industry/application oriented.

The primary use of niobium is to improve the wear resistance and this has been described in this paper for a variety of different cast irons. Without doubt this is a big application for the future. Mining, off shore, the automotive industry, steel and non-ferrous rolling mills are only some industries that should take more benefit from this research and development.

It is the strong belief of the author that the use of niobium in cast iron has a massive potential for the future. We are still in the very beginning of this development and there is still a lot of work to do. The foundry industry and its customers are no exception from other industries in that there is a strong resistance against new alloys and materials, production methods and

product applications. By working together, R&D, production, sales & marketing should be able to convince customers that they will benefit strongly from niobium alloyed cast irons of all kinds.

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