

## TECHNOLOGY, PROPERTIES AND APPLICATIONS OF NIOBIUM CARBIDE REINFORCED STEEL AND IRON ALLOYS

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### Abstract

The large cost and considerable downtime caused by replacing worn parts in earth moving and mining equipment, as well as in the materials processing industry, represents a continuous challenge to material development. Components designed for sacrificial wear must in the first place possess adequate abrasion resistance. Frequently, however, they must also have the ability to withstand impact and to resist chemical attack. The requirement of good abrasion resistance in combination with good toughness is generally in contradiction. Typically, hard iron-based materials such as martensite or ledeburite are highly resistant to abrasion, yet very brittle and difficult to machine. An innovative approach is to compose a more ductile iron-based matrix, embedding a much harder wear resistant phase. Amongst those extremely hard phases are carbides of the transition metals titanium, niobium, and tungsten with hardness of over 2000 HV. Particularly, NbC is a very interesting hard phase since its hardness is one of the highest among the transition metals carbides and its density is very similar to that of molten iron, so that gravity segregation effects in the liquid phase are small. Volume fractions up to 35% of NbC can be formed *in-situ* as primary carbide in the liquid phase or added externally using a FeNbC master alloy. The latter approach is particularly applicable when higher amounts of NbC need to be added. Molybdenum additions are important to adjust the properties of the matrix towards high toughness and good ductility. This paper elucidates the strategies and possible technologies of achieving such composite materials and demonstrates several examples of applications along with the achieved sustainability benefits. In particular, fundamental and tribological properties of NbC are presented.

### Introduction

The enormous, and at the same time, increasing cost of replacing worn parts in earth moving and mining equipment, as well as in the materials processing industry, represents a continual challenge to material development. Components designed for sacrificial wear must possess, first of all, adequate abrasion resistance. Frequently, however, they must also have the ability to withstand impact and to resist chemical attack. The requirement of good abrasion resistance, in combination with good toughness, is generally rather restrictive. Typically, a material that is highly resistant to abrasion is at the same time hard and brittle.

Wear is defined as the gradual and progressive loss of material due to the relative motion between the active body and a counter-body. Two basic principles can be involved in removing material from the surface: Material can be disintegrated and detached mechanically or by chemical reaction, both actions occurring at the surface. Wear resistance of a material is a system property and not a material property. It is controlled by a multitude of parameters consisting of material and counter-body properties, contact stresses and the environment. Therefore, wear performance can only be evaluated by simulating the real-life situation as closely as possible. Nevertheless, standardized procedures for benchmarking abrasion resistance have been developed, like the rubber wheel test according to ASTM G65.

Abrasion is a form of wear that is mediated by hard particles covering a wide range of sizes. This statement should be qualified to indicate that while the severity of abrasion is expected to increase as the hardness of the particles increases, abrasive wear is not necessarily eliminated if the particles are soft. The particles are almost always mineral substances that are being handled for some engineering or industrial purpose, or that have penetrated into a machine or system as foreign contaminants.

Since solid-liquid mixtures are often handled in the mining industry, the combined effect of abrasion and corrosion must be considered. It is easy to see how abrasive particles can affect corrosion rates by removing protective films and exposing fresh metal to the environment. These films take time to rebuild, and if they are continually destroyed by an abrasion action of slurry, corrosion rates can increase drastically.

Figure 1 compares representative hardness values of mineral species with that of technical alloys. It is evident that many minerals are much harder than standard construction materials, for instance steel or aluminum. Only super hard compounds like carbides of the transition metals represented by groups IVB to VIB in the periodic table of elements, amongst them also molybdenum, can compete with the hardest minerals. Yet these carbides cannot be processed into large-scale components and are also very brittle and expensive. However, they can be dispersed to a certain fraction into a metallic matrix, like a steel or a cast alloy. Another possibility is to clad them on the surface of a metallic substrate by welding or other coating processes. Still, these remain expensive manufacturing processes that also have limitations with regard to component size. For the bulk of applications, abrasive resistant steel is the material of choice. It is available as heavy plate or as hot-rolled strip, allowing the manufacture of large component sizes in an economical way. Typical abrasion resistant steel grades cover a hardness range of 300 to 600 on the Brinell scale. Abrasion resistant steel has a guaranteed high hardness across the entire plate thickness so that its resistance to wear remains adequate, even when material loss has progressed. Thus, it is the material of choice for components exposed to sacrificial wear. Carburizing steel is an alternative material for those applications where wear occurs but dimensional stability of the component should be maintained. The very hard surface layer of carburized steel extends only over a few millimeters at the most. Such material is mainly used for gear and drive systems in equipment exposed to pollution by abrasive particles.

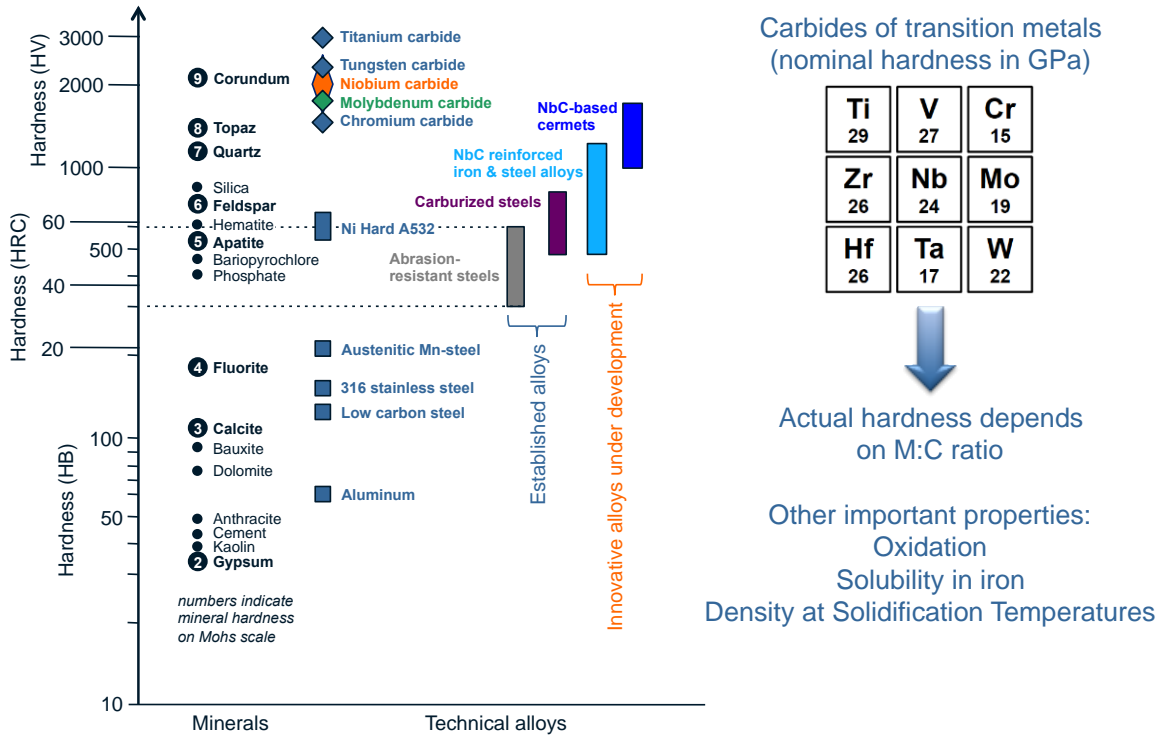


Figure 1. Hardness of mineral species compared to hardness of technical alloys.

### Abrasion Resistant Steel

Abrasion-resistant steels are designed to withstand wear that is caused by friction or by the impact of materials, such as minerals, sand or gravel. Abrasion resistance generally increases with hardness of the active body, avoiding scratching and plowing by hard counter-body species. Fatigue strength and toughness are additional properties coming into play, especially when dynamic or impact loads are acting on the active body. Thirdly, some applications may additionally require temperature and oxidation resistance. Accordingly, different abrasion resistant steel classes have been developed. Abrasion resistant steel grades are usually classified based on their hardness levels ranging from 300 up to 600 HB. The standard class focuses primarily on surface hardness and is represented by unalloyed CMn steels. Alloyed steel grades combine hardness with guaranteed toughness and also allow production of heavier gages. Alloyed steel grades with low-carbon equivalent provide increased toughness at lower temperature and simultaneously improved weldability. Super abrasion-resistant grades have a further improved abrasion resistance by incorporating hard second phases in a moderately hard matrix. With the exception of the standard grades, molybdenum is a vital alloying element in achieving the desired property mix.

In addition to the wear-resistant characteristics of steel, such as hardness, work hardening, resistance against crack formation and propagation, the following application oriented criteria need to be considered as well in the selection procedure:

- Toughness;
- Weldability;
- Hot and cold forming capability;
- Machinability;
- Cost-benefit ratio.

Table I. Typical Applications for Abrasion Resistant Steel Grades

Heavy Vehicles and Earth Moving Equipment	<ul style="list-style-type: none"> <li>• Bulldozer shovels and buckets</li> <li>• Slush plates for bulldozers</li> <li>• Exterior linings of bulldozer buckets</li> <li>• Trailer beds</li> <li>• Vessels for dump and cargo trucks</li> <li>• Dredger buckets</li> </ul>
Cement and Mining Industry	<ul style="list-style-type: none"> <li>• Lining and paddle material for ready-mixed concrete turbine mixer</li> <li>• Conveyor chute for concrete mixing plant</li> <li>• Pug mill for soil cement</li> <li>• Conveyor pipe for solids (pneumatic pipelines for coal mines)</li> <li>• Lining and grates for ball mills</li> <li>• Lifters for Semi-Autogenous Grinding (SAG) mills</li> </ul>
Chemical Industry	<ul style="list-style-type: none"> <li>• Agitators for asphalt plants and finishers</li> <li>• Sand conveyor pipe for sand cracking in naphtha cracking plants</li> <li>• Sulfide mineral bucket elevators</li> </ul>
Metallurgical Industry	<ul style="list-style-type: none"> <li>• Chutes and liners</li> <li>• Ore screens</li> <li>• Lining for rotary mixers and conveyor belts</li> <li>• Raw material and roll feeders</li> </ul>
Others	<ul style="list-style-type: none"> <li>• Earth drills</li> <li>• Shear liners</li> <li>• Tunnel boring machines</li> <li>• Agricultural equipment</li> </ul>

## Microstructural Influence on Wear Resistance

The microstructure of steel plays a critical role with regard to its wear performance. For the same hardness, austenite is more abrasion resistant than ferrite, pearlite or martensite due to the higher strain hardening capacity and ductility of austenite [1]. In steels with less than 1.0% carbon, bainitic microstructures have the highest wear resistance, followed by quenched and tempered microstructures, annealed structures and spheroidized structures, all at the same hardness level [2]. Figure 2 summarizes the effects of steel hardness and microstructures on wear resistance [3]. Figure 3 shows the relationship between hardness and the abrasion resistance ratio [4]. The abrasion resistance was evaluated according to ASTM G65 using silica ( $\text{SiO}_2$ ) as the abrasive. The abrasion resistance was calculated as the ratio of the weight loss of mild steel to the weight loss of abrasion-resistant steel. Analyzing ferritic-pearlitic and martensitic microstructures under the same test conditions reveals a distinctly different impact of the hardness on the wear rate [5]. As shown in Figure 4, hardness increase in a ferritic-pearlitic microstructure results in only a minor improvement of wear resistance. In martensitic steel, on the contrary, increasing the hardness leads to substantial gains in wear resistance. This difference appears to be the consequence of different wear mechanisms acting in both steels. The soft ferrite phase present in ferritic-pearlitic steel is plastically deformed by the indentation of hard particles in the near-surface region leading to work hardening, (Figure 5). Low-cycle fatigue can induce cracking in the work-hardened zone and detach particles. Another mechanism of material removal is caused by adhesion on the abrasive particle.

As-quenched martensitic steel has very high hardness and does not include the presence of a soft, deformable phase. Upon indentation of hard particles into the surface of martensitic steel, micro-cracks can form. When several adjacent micro-cracks link up, a wear particle can be cut loose. Several effects are available to raise the resistance against this crack-based wear mechanism. (1) Increasing the steel hardness raises the elastic limit stress of the material reducing the formation of cracks. (2) Refining the microstructure obstructs the propagation of existing cracks, in particular, increasing the number of large angle grain boundaries. (3) Embedding ultra-hard special carbide phases in the martensitic matrix can carry the highest contact stresses without fracturing. It is important that the size of these carbide phases is big enough compared to the size of the abrasive counter-body to prevent them from being removed by particle plowing. The hard phase can consist of molybdenum or chromium carbides formed during tempering, as well as of primary niobium or titanium carbides that have formed already before rolling. The latter primary carbides are much larger in size than the carbides formed *in situ*. Figure 3 indicates that such a composite material has superior abrasive wear resistance in spite of a relatively moderate hardness of its martensitic matrix.

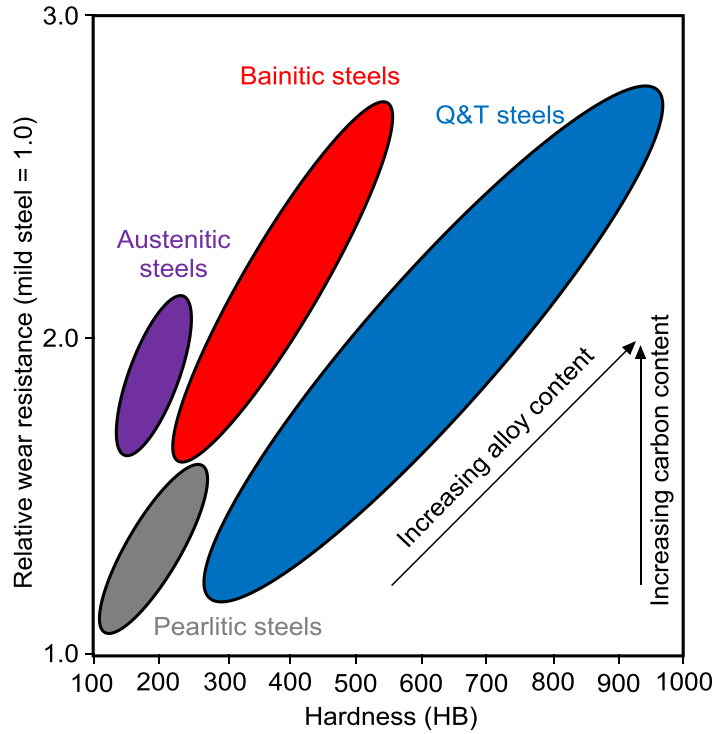


Figure 2. Influence of microstructure and hardness on wear resistance compared to mild steel.

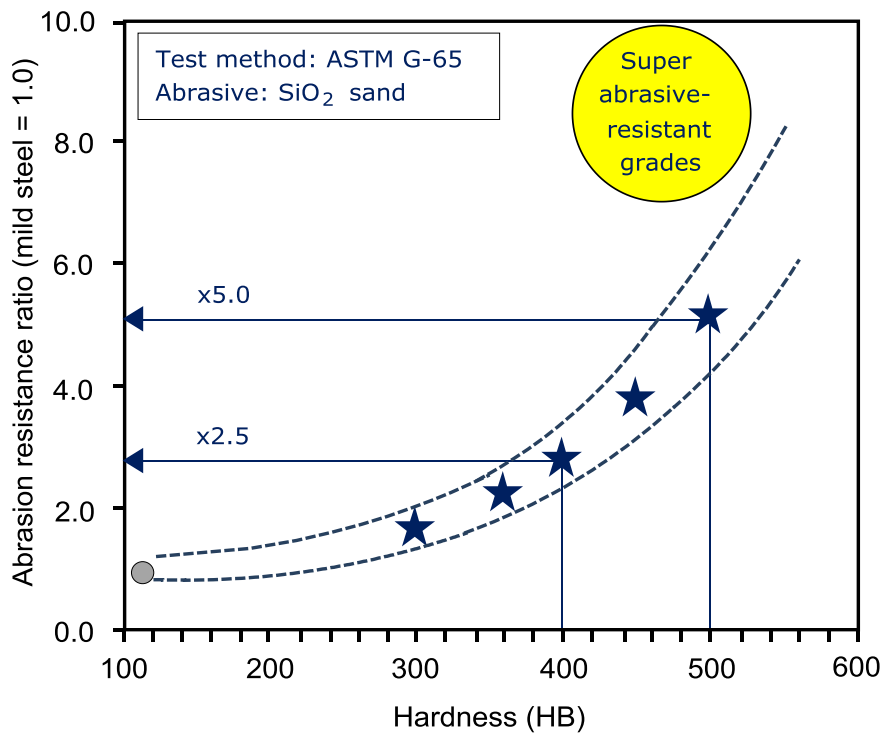


Figure 3. Performance of typical abrasive resistant steel grades and potential of super-abrasive resistant grades.

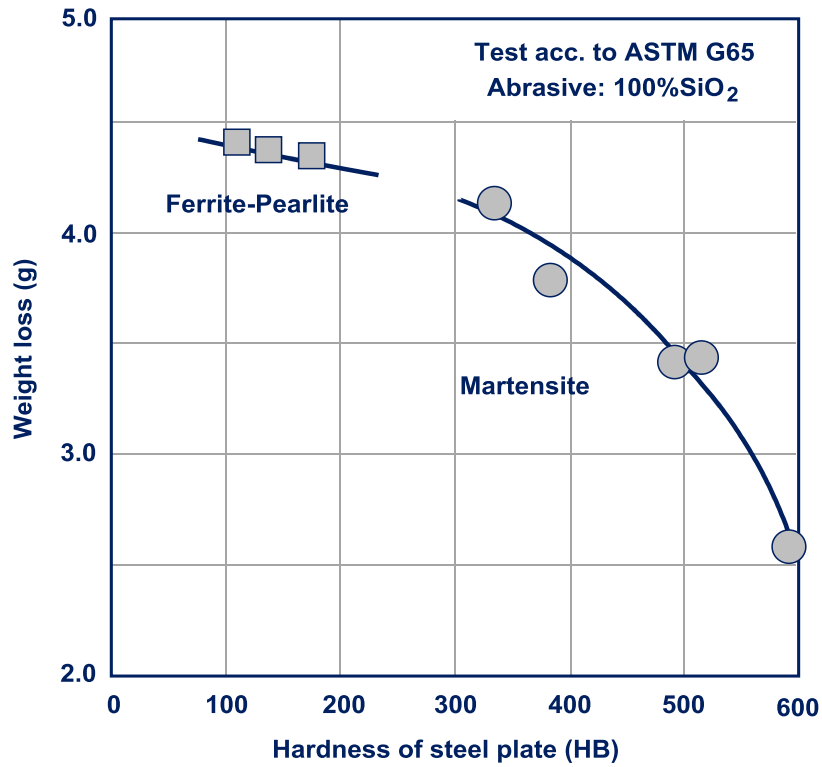


Figure 4. Relationship between hardness, microstructure and weight loss in rubber wheel test.

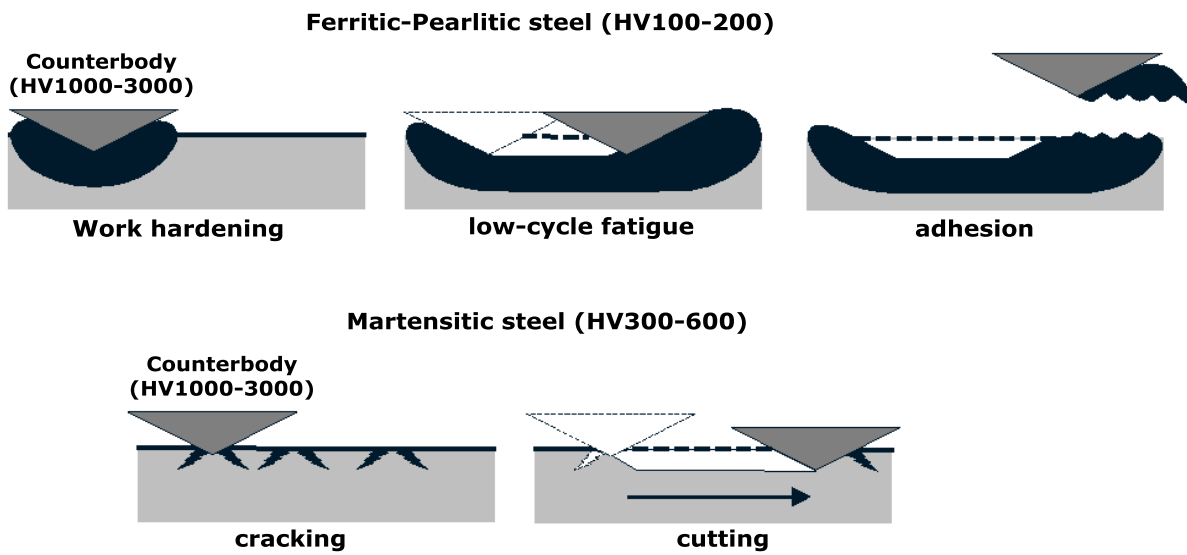


Figure 5. Schematic hard particle wear mechanisms in ferritic-pearlitic and martensitic steels.

## Conventional Abrasion Resistant Steels

Conventional abrasion resistant grades are mainly water quenched carbon-manganese steels, often microalloyed with a small amount of boron. In such steel, hardness is determined directly by the carbon content [6]. In the range of up to around 0.40 mass percent carbon, the hardness nearly linearly increases with the carbon content, (Figure 6). However, with increasing hardness the toughness of the quench hardened steel decreases to very low values, (Figure 7). For standard wear resistant grades toughness is not specified and quenched carbon-manganese steel with the required hardness suffices. Nevertheless, toughness in such grades can be improved by several metallurgical measures. Refining the microstructure, ie. particularly the large angle boundary structure, is effective in obstructing crack propagation as will be explained later. Other positive measures are keeping the impurity levels of phosphorous, sulfur and nitrogen low, as indicated in Figure 7. Tempering is another way of increasing toughness, but in such unalloyed grades it simultaneously results in a significant drop of hardness and thus wear resistance.

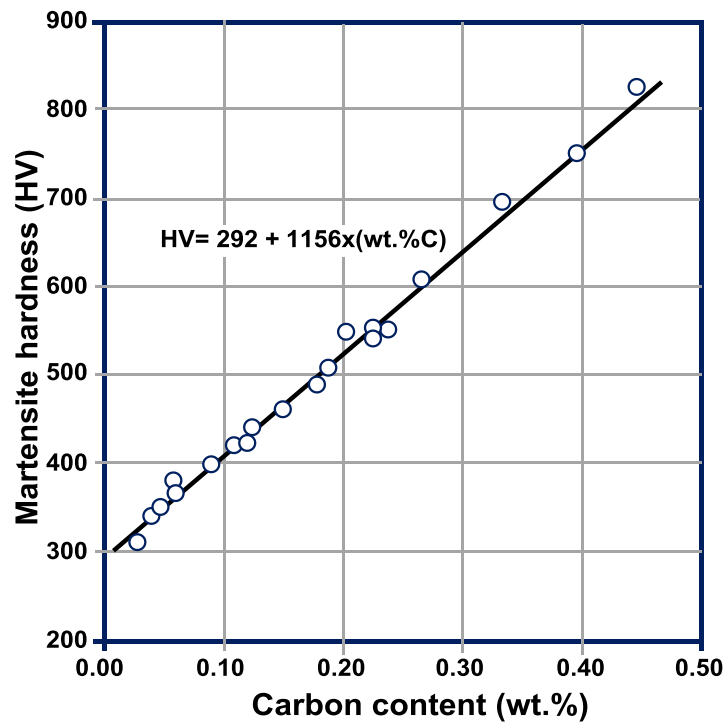


Figure 6. Relationship between carbon content and hardness of fully quenched martensite.



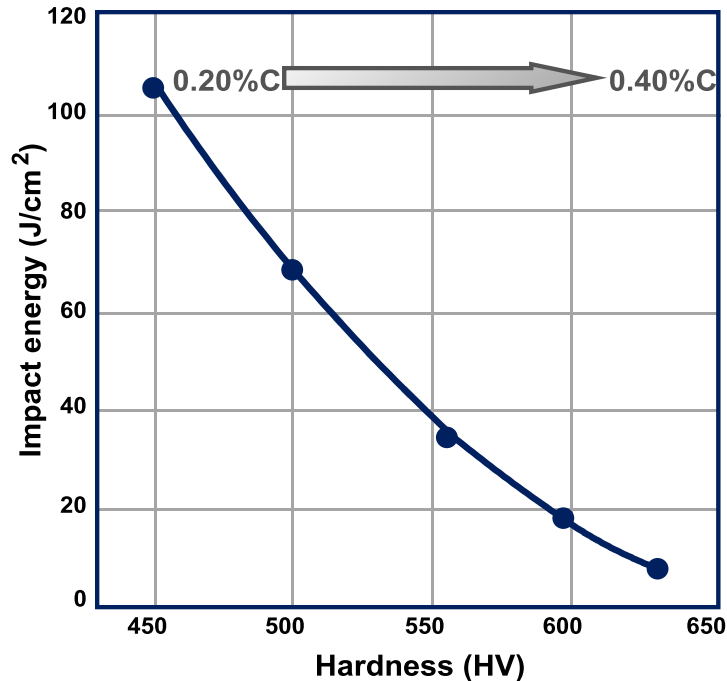


Figure 7. Influence of hardness on impact toughness in fully quenched martensitic steel.

#### Microstructural Optimization of Martensitic Steel

A key parameter in refining the microstructure of martensitic steel is the prior austenite grain size (PAGS) because the martensitic substructure develops within that perimeter. A prior austenite grain contains a very large number of discrete laths of dislocated martensite. These are organized into packets, in which the laths share the same habit plane. The packets are often subdivided into blocks in which the parallel laths are the same crystallographic variant of the martensitic transformation. Since packet and block boundaries are high angle boundaries, these constituents are considered to be effective grains. In other words, the strength and toughness of lath martensitic steels are strongly related to packet and block sizes. It is known that both the block width and the packet size are proportional to the prior austenite grain size [7,8]. For a very fine prior austenite grain size the packet size approaches that of the prior austenite grain size. The packet size can be considered a good approximation of the effective grain size relevant for toughness and critical fracture stress, (Figure 8).

Several measures can be taken for reducing the PAGS. A relatively low reheating temperature, possibly combined with Ti-microalloying leading to small TiN particles, can limit the austenite growth during long residence time in the furnace. Microalloying by niobium in combination with low finish rolling temperature contributes to refinement of austenite grains through a grain boundary drag effect caused by atoms in solid solution and a pinning effect due to *in-situ* precipitation. That solute drag effect is enhanced by the simultaneous presence of molybdenum. The austenite grain does not recrystallize and is pancaked resulting in a fine-sized ferritic-pearlitic microstructure upon cooling. In the subsequent heat treatment cycle, that refined microstructure is re-austenitized and then quenched into martensite. During the re-austenitizing phase, finely dispersed Nb or NbMo precipitates effectively prevent coarsening of the austenite

grains as demonstrated by Figure 9. This grain size controlling effect is stable over a substantial temperature range and disappears only when temperatures exceed the dissolution temperature of the particles. Over the entire austenitizing temperature range, microalloyed steel provides a smaller PAGS. The difference to conventional steel becomes bigger with increasing austenitizing temperature, (Figure 10). The smaller PAGS with the resulting refined martensitic substructure has evident benefits for the mechanical properties of the steel. Especially the low temperature toughness is substantially improved, as indicated by Figure 11 [9]. A disadvantage of PAGS refinement in unalloyed carbon steels is that hardenability reduced. The grain refined austenite structure renders a higher residual fraction of ferrite upon quenching at the same cooling rate.

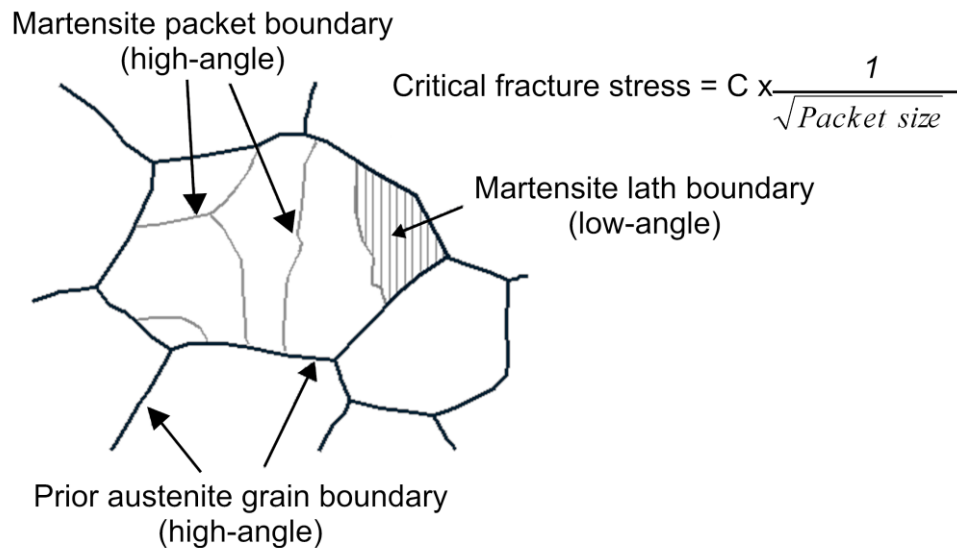


Figure 8. Martensitic substructure developing in the prior austenite grain and relationship of the critical fracture stress to the packet size.

PAGS after austenitizing at 950 °C

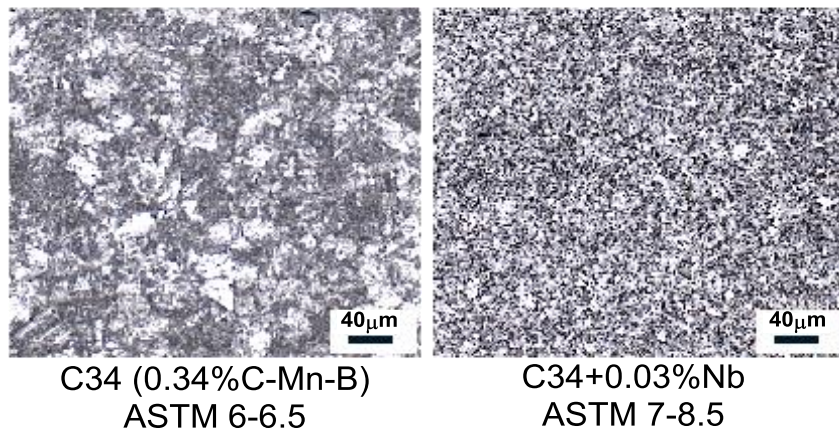


Figure 9. Refinement of prior austenite grain structure in a plain CMn C34 grade (0.34%C) by Nb-microalloying.

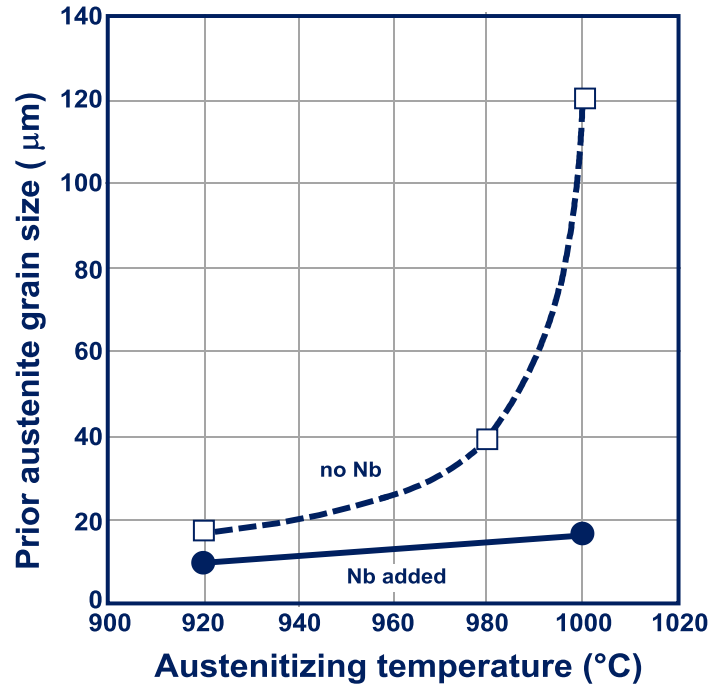


Figure 10. Relationship between prior austenite grain size (PAGS) and reheating temperature before quenching.

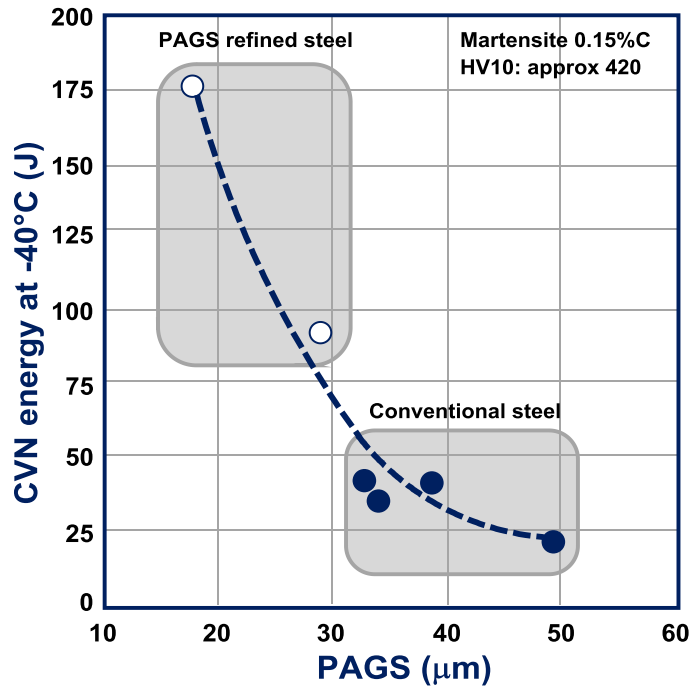


Figure 11. Influence of the prior austenite grain size on the impact toughness (test temperature -40 °C) for fully quenched martensite with 0.15%C.

## Alloyed Abrasion Resistant Steels

Alloyed steel types are being applied where toughness matters and where through-hardening at heavier gages is required. Guaranteed minimum toughness (eg. 21 J or 27 J) can be adjusted at low temperature (eg. 0 °C or -40 °C) by controlling the carbon content and the alloying concept in combination with appropriate heat treatment. Such grades comprise an enhanced service lifetime in applications where impact loads are prevailing, especially in cold climates.

In conventional carbon-manganese steel the hardening depth is limited to a few millimeters. However, for specific applications, plate gages of up to 100 mm are required. Thus, a precisely tuned amount of alloying elements in combination with high cooling rates is required to achieve a high hardness value in the core of thicker plate and to obtain a homogeneous microstructure. Even though surface hardness is easily achieved by a quenching treatment, hardness tends to decline towards the core of a heavy gaged steel plate. Therefore, hardenability needs to be enhanced by alloying elements like manganese, molybdenum, chromium, copper and nickel. In estimating hardenability by Grange's technique [10] it is assumed that the hardenable diameter for iron is zero. The influence of single alloying elements on the change of the hardenable diameter can be estimated from Figure 12. Besides carbon, molybdenum has the strongest effect before manganese and chromium. Accordingly, adding 0.25%Mo to the Fe-0.2 %C base alloy would increase the hardenable cylinder diameter with 90% martensite at the center, by approximately 8 mm.

For a first judgment of the achievable hardening depth, the traditional Grossman relationship is often applied [11]. Accordingly, the hardenability of an alloyed steel characterized by the critical diameter  $D_I$  can be calculated based on the critical diameter of the iron-carbon base composition ( $D_{IC}$ ) and multiplying factors ( $MF$ ) for each alloyed element. As mentioned before, a smaller austenite grain size reduces the base hardenability.

$$D_I = D_{IC} \times MF_{Si} \times MF_{Mn} \times MF_{Cr} \times MF_{Mo} \times MF_{Ni} \times MF_V \times MF_{Cu} \times MF_B \times 25.4 \text{ (mm)}$$

$$D_{IC} = (C/10)^{1/2} \times (1.70 - 0.09N) \text{ with } C: \text{ carbon content and } N: \text{ austenite ASTM grain size number)}$$

The multiplying factors given by Murota et al. [9] for each alloying element can be used in most cases:

- $MF_{Si} = 0.70Si + 1$
- $MF_{Mn} = 3.33Mn + 1$
- $MF_{Cr} = 2.16Cr + 1$
- $MF_{Mo} = 3.00Mo + 1$
- $MF_{Ni} = 0.36Ni + 1$
- $MF_V = 1.75V + 1$
- $MF_{Cu} = 0.35Cu + 1$
- $MF_B = 1.3$  (B added) or 1.0 (without B addition)

The addition of boron is an efficient method of increasing the hardenability, particularly for lower strength grades, allowing the use of very lean steel compositions. For higher grade abrasion resistant steels more carbon and other alloying elements need to be added for attaining the required mechanical properties. Besides manganese being a standard alloying element, molybdenum is particularly efficient in providing good hardenability. Molybdenum's effect is demonstrated in Figure 13 for steel with a base composition of 0.5%Mn and 0.3%Si at carbon levels of 0.19% and 0.42%, respectively, using the Jominy test.

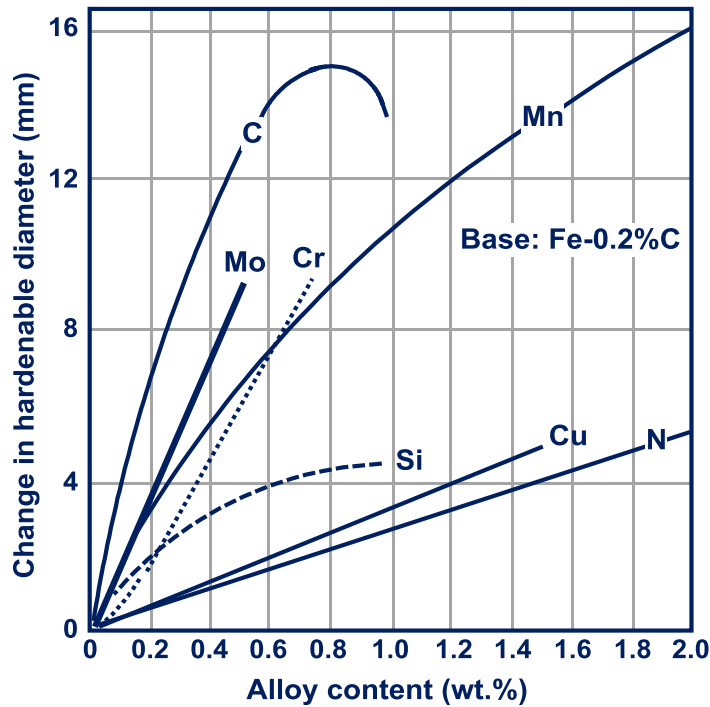


Figure 12. Influence of single alloying elements on the change of the hardenable diameter using Grange's technique [10].

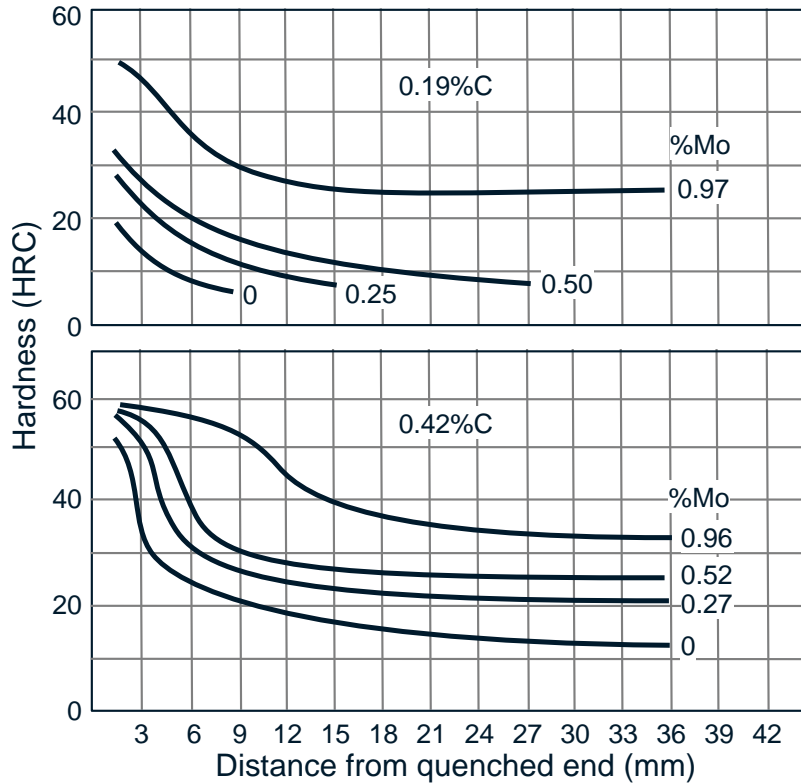


Figure 13. Effect of molybdenum and carbon on the Jominy hardenability curves of steels containing 0.5% Mn and 0.3% Si.

The Grossmann relationship is based on the assumption that there are no interactions between carbon and the alloying elements or between the various alloying elements. However, from Figure 14 it becomes evident that molybdenum's multiplying factor varies with the carbon content [12]. Especially on the low-carbon side, which is most relevant for abrasion resistant steels, the multiplying factor decreases with increasing carbon content, reaching a minimum at around 0.45% C. That means molybdenum is particularly effective in raising the hardenability of abrasion resistant steel with reduced carbon equivalent (CE). Low CE steel is preferred for its superior impact resistance at cold temperatures and its simultaneously improved weldability. The amount of molybdenum needed naturally depends on the plate gage to be produced. Thicker plates require a larger molybdenum addition. Especially at lower carbon levels, the molybdenum multiplying factor also strongly depends on the PAGS [12]. When the grain size decreases, as is the case in the Nb-microalloyed steel concept in combination with controlled rolling, the multiplying factor increases progressively, (Figure 15). Thus molybdenum alloying can effectively counteract the loss of hardenability caused by grain refinement.

With regard to further increasing hardenability, the combination of molybdenum with chromium appears to have a strong synergy. The combined effect of these two elements is much stronger than that of manganese and chromium, (Figure 16). Accordingly, the production of heavy gaged abrasive steel typically relies on combined alloying of molybdenum and chromium. The further addition of nickel and boron may become necessary to ensure a uniform property profile in the through thickness direction for grades in the high hardness range (500-600 HBW). Table II indicates representative ranges of alloying elements for abrasion resistant grades of different hardness levels, and their Cold Cracking Susceptibility Parameters, CET, at two gages. The actual alloying concept largely depends on the possibilities and preferences of the particular steel mill. In general, it is aimed to keep the carbon content as low as possible at a given target hardness and gage to optimize toughness and weldability. Thus, carbon ranges from 0.15% to nearly 0.5% over the product spectrum. Chromium addition of up to 1.5% has proven to be very effective against wear in weakly acid media enhancing the wear life by more than 35% [13]. Toughness and cold-forming behavior as well as resistance to impact wear are increased by grain refinement due to Nb-microalloying, (Figure 11). Comparing a standard 450 HBW grade with a Nb-microalloyed variant under abrasive wear by hard minerals revealed that the service life can be increased by around 20% [14].

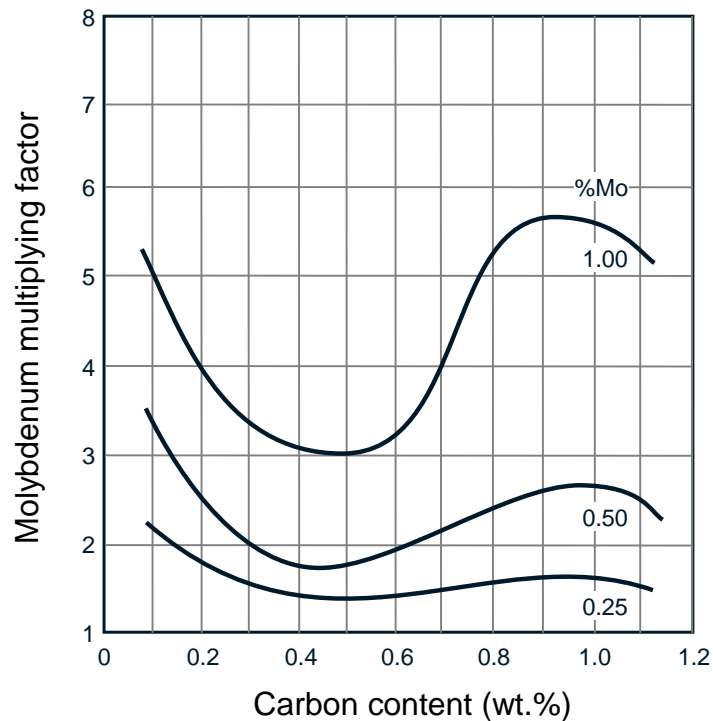


Figure 14. Effect of molybdenum and carbon on the molybdenum multiplying factor of steels containing 0.5%Mn and 0.3%Si.

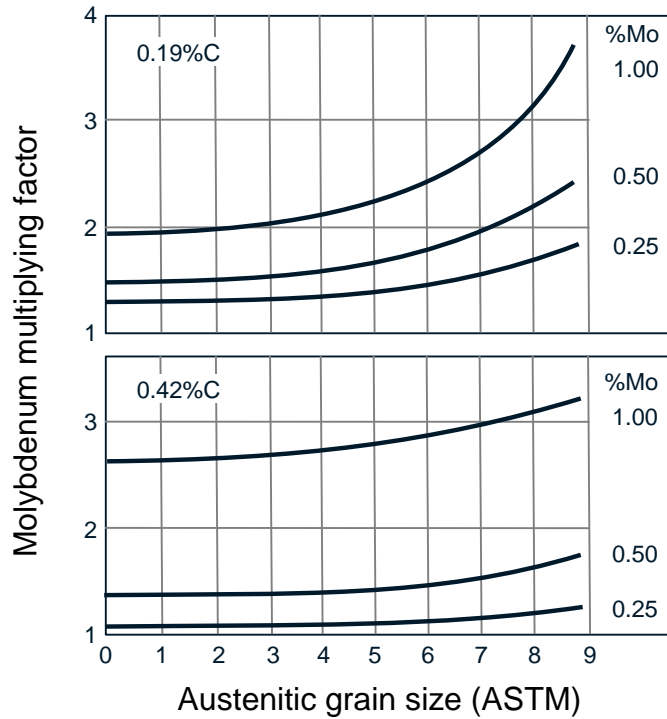


Figure 15. Effect of austenite grain size on the molybdenum multiplying factor of steels containing 0.5%Mn and 0.3%Si.

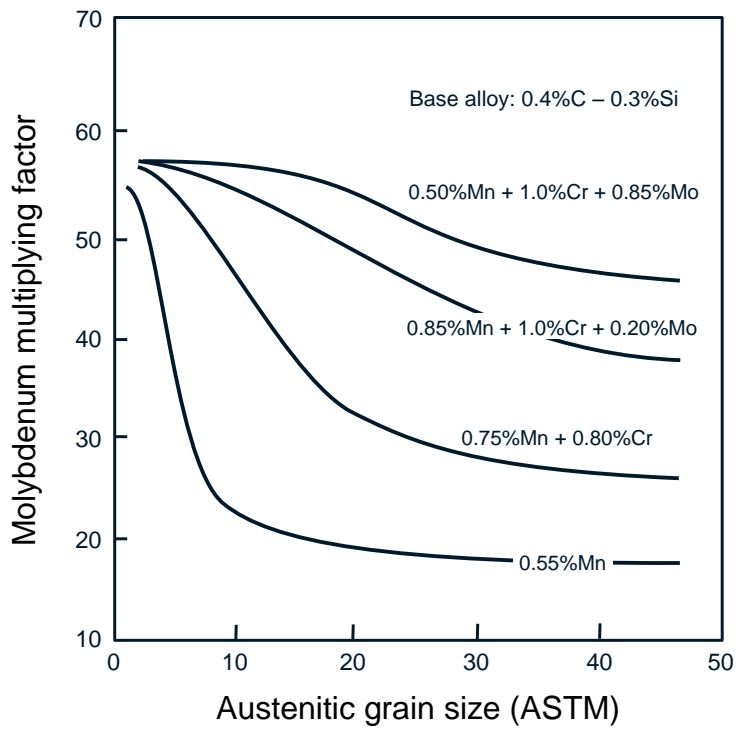


Figure 16. Effect of alloying elements on the Jominy hardenability curves of steel containing 0.4%C and 0.3%Si.



Table II. Typical Chemical Composition of Abrasion Resistant Steel Grades in the Range of 400-600 HB

Target hardness (HB)	Max. plate gage (mm)	Chemical composition (max. %)						Typ. CET (%) at gage	
		C	Si	Mn	Cr	Ni	Mo	8 mm	40 mm
400	100	0.20	0.80	1.50	1.00		0.50	0.26	0.37
450	100	0.22	0.80	1.50	1.30		0.50	0.38	0.38
500	100	0.28	0.80	1.50	1.00	1.50	0.50	0.41	0.41
600	40	0.40	0.80	1.50	1.50	1.50	0.50	0.55	0.55

### Abrasion Resistant Steels Containing Hard Phases

Embedding ultra-hard particles in a relatively softer steel matrix can further increase the abrasion resistance, (Figure 17). Such embedded hard particles consist typically of transition metal carbides, such as those of titanium, niobium, vanadium, tungsten, molybdenum or chromium, of which the hardness is indicated in Figure 1. Titanium and niobium have a very low solubility product and hence tend to form carbides already in the liquid phase or during solidification. *In-situ* formed primary carbides can achieve a relatively large size of tens of micrometers. All carbide-forming elements can also precipitate as secondary carbides in the steel matrix under suitable tempering conditions. These secondary carbides are typically less than 100 nm in size. Secondary carbides have the potential to raise the strength and hardness of the steel matrix, especially when their size is smaller than 10 nm. Molybdenum has a relatively good solubility in steel. Nevertheless, it can participate to some extent in primary titanium or niobium carbides [15,16]. Typically, molybdenum appears as secondary precipitates after a tempering treatment, contributing to strength and hardness increase of the steel matrix. The larger-sized primary carbides act as hard barriers in the surface and are load bearing to abrasive particles. As such they can interrupt particle plowing or even break an abrasive particle, as indicated by Figure 18, resulting in reduced chipping and material loss.

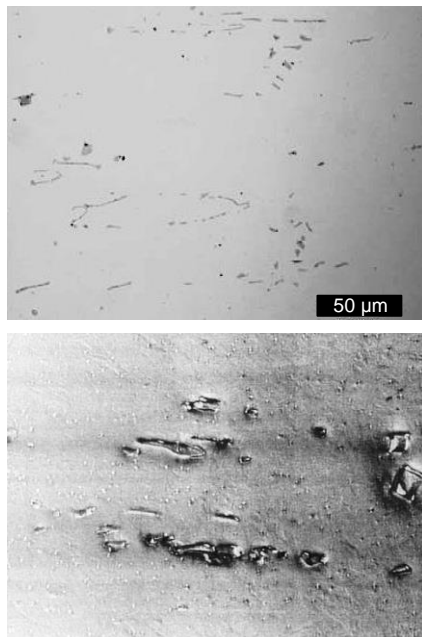


Figure 17. Micrographs of *in-situ* precipitated primary TiC particles in martensitic steel matrix.

## Steel matrix containing carbide particles

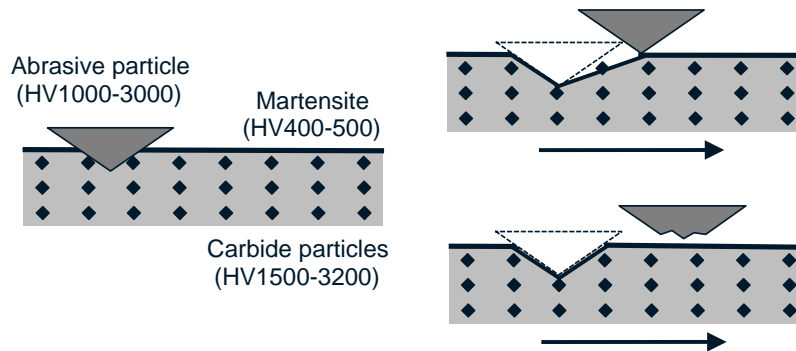


Figure 18. Schematic effect of superhard particles embedded in a martensitic steel matrix on abrasive wear resistance.

One alloying strategy is primary precipitation of transition metal carbides from the melt using appropriate element concentrations. Thereby the addition of carbide former and carbon has to correspond to the stoichiometric ratio. For instance 0.15 weight percent of carbon is needed to fix 0.6 weight percent of titanium forming  $\text{TiC}$ , since the stoichiometric ratio (by atomic weight) is around 1:4. That means the initial carbon content in the steel melt must be enhanced to around 0.4% when the target carbon content of the final steel matrix is intended to be 0.25 percent. Because titanium causes technical casting problems owing to its high affinity for oxygen, and vanadium has a relatively high solubility in the steel matrix, niobium appears to be a particularly interesting carbide forming element in alloy design. Another important aspect with regard to the final material properties is the carbide morphology. Compact shaped carbide particles that are not too large in size and that are homogeneously distributed are preferable. Large carbides with a dendritic three-dimensional morphology are disadvantageous with regard to fracture mechanics and toughness. Favorable carbide morphology can be achieved by optimizing carbide nucleation conditions and dwell time in the ladle [17]. However, when adding higher amounts of carbide former to liquid iron it becomes generally difficult to control shape and size of the *in-situ* forming carbide. Hence the addition of niobium in such alloys has typically been restricted to a few weight percent thus far.

### Addition of NbC Particles as Hard Phase in Iron-based Alloys

A possible solution for introducing higher amounts of hard carbide phase into iron-based alloys is to add already formed carbides with defined size and shape to the liquid phase. This requires that firstly the carbide does not melt and secondly does not dissolve in the liquid iron bath. NbC fulfills both requirements. Its melting point is  $3522\text{ }^{\circ}\text{C}$  and its solubility is exceptionally low. Another very beneficial property is the density of NbC, around  $7.7\text{ g/cm}^3$ , being very similar to that of liquid iron. Consequently gravity segregation of solid NbC added to liquid iron is quite limited contrary to other hard carbides like  $\text{TiC}$ , VC (lighter) or WC (heavier). Furthermore, VC and WC also have an appreciable solubility in iron. To avoid segregation and solubility issues, sintering routes have been developed to produce iron-based alloys with high contents of hard phases. An example is ferro-titanite where powders of FeTi mixed with a matrix alloy and graphite is forming *in-situ* a  $\text{TiC}$  rim structure having a core of martensitic steel, (Figure 19).

Apart from being a rather expensive production route, sintering routes have limitations in size and geometry of parts as compared to castings.

A recently developed innovative ferroalloy type developed by CBMM comprises an iron matrix with embedded NbC particles, (Figure 20). This ferroalloy can be directly produced during alumino-thermic reduction of Nb-oxide in the presence of iron and carbon. The primary NbC particles formed in this process have a compact blocky shape and are typically in the size range of 5 to 20  $\mu\text{m}$ . The volume fraction of particles in the ferroalloy is around 50%. This ferroalloy as such can be considered as a metal-matrix composite (MMC) and has an extremely high wear resistance. When adding it to the ladle the iron matrix will melt and release solid NbC particles into the metal bath. The volume fraction of NbC can thus be diluted to any level below 50%. The shape and size of the carbide will only marginally change if at all due to the low solubility of NbC. In this way, larger amounts of carbide having a compact morphology can be introduced to a cast alloy.

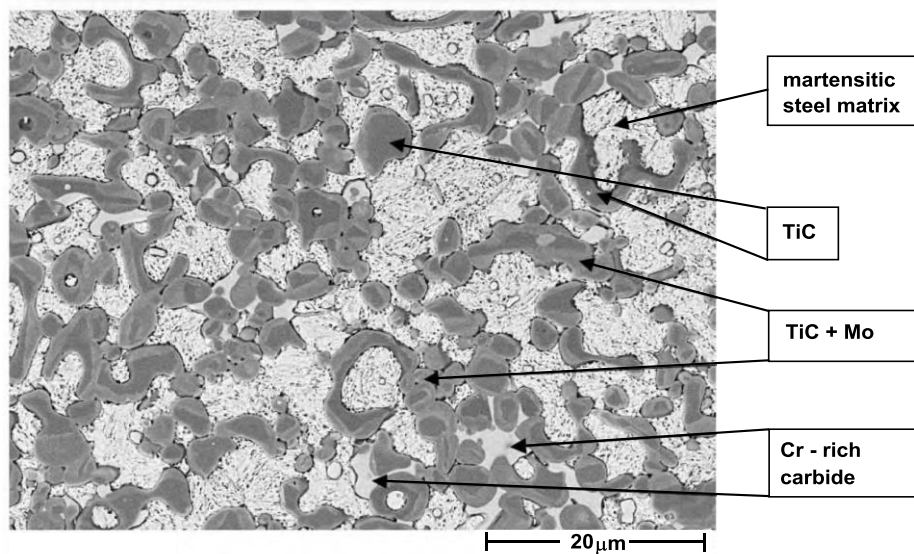


Figure 19. Microstructure of ferro-titanite WFN grade [18].

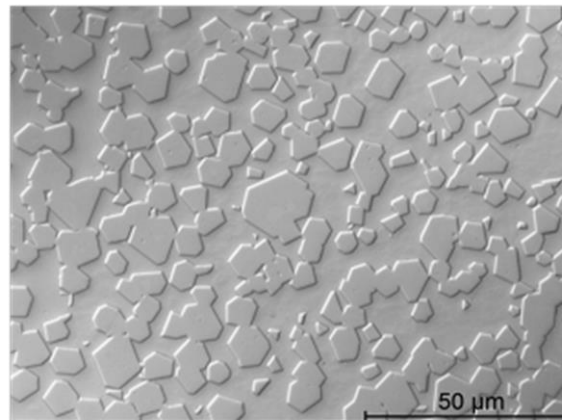


Figure 20. Microstructure of a ferroalloy with iron matrix containing primary NbC.

## Metallurgical Functionality of Niobium and Molybdenum Alloying in White Cast Iron

White cast iron (WCI) is a well-established material for many applications requiring high hardness and wear resistance. Over the years different grades of WCI have been developed, ranging from conventional white cast iron to Ni-hard, Ni-resist and high chromium white cast iron. High Cr WCI offers the best balance of hardness and toughness of all these due to an optimized balance of carbide type and morphology. Nickel-chromium white irons develop carbide types like  $\text{Fe}_3\text{C}$  or  $(\text{Fe,Cr})_3\text{C}$ . The hardness of these carbides is comparable to that of quartz. In chrome-molybdenum white irons a primary  $(\text{Cr,Fe})_7\text{C}_3$  carbide is being developed with a hardness of nearly twice that of quartz. The  $(\text{Cr,Fe})_7\text{C}_3$  carbides in chrome-molybdenum white irons are embedded in an austenite/martensite matrix providing the higher toughness.

A typical representative of chrome-molybdenum white irons is Climax 15-3 or variations thereof. The hardness of the primary carbide in the high-alloy white irons is about twice that of silica, most often the primary gang material in the ore that is being processed, resulting in superior abrasion resistance. Figure 21 shows a comparison of the linear abrasion rate of various cast irons after testing in a silica-based slurry [19]. The superior performance of the chrome-molybdenum white iron is reflected in the lowest abrasion rate.

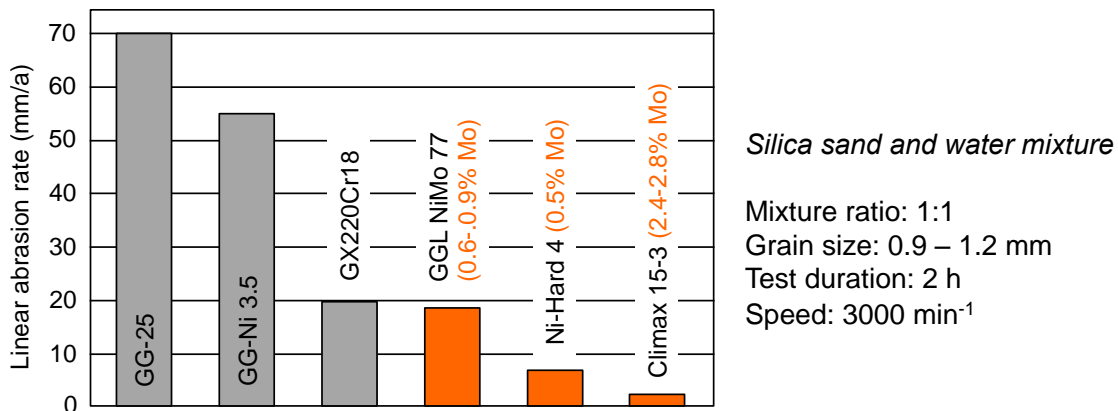


Figure 21. Abrasion rates of various cast materials exposed to hydro-abrasive wear in a silica-based slurry [19].

Molybdenum is primarily used to stabilize the austenite phase during cooling after solidification, as well as to prevent the formation of pearlite. One of the major advantages of molybdenum is that it has little effect on the  $M_s$  temperature, compared with other elements that tend to decrease the  $M_s$  temperature and over-stabilize the austenite. Molybdenum contents of less than about 1.0% are insufficient to suppress pearlite formation in heavy section castings, while amounts greater than 3.0% have no additional benefit in suppressing pearlite formation. Molybdenum partitions partly into austenite and partly into  $M_7C$  as well as  $MC$  carbides [20]. With molybdenum alloy additions below 1%, that proportion partitioned into austenite becomes too low to effectively suppress pearlite formation. Niobium was found to enhance the pearlite retarding effect of molybdenum when alloyed in combination in high chromium iron. This synergistic effect saturates above niobium additions of 1%, (Figure 22) [21].

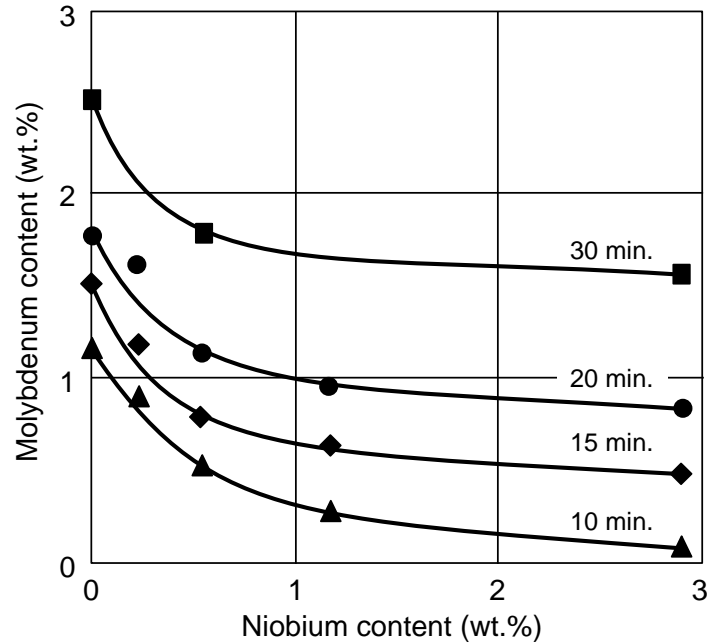


Figure 22. Combined effect of niobium and molybdenum alloying on the time required for 5% pearlite formation at a temperature of 700 °C in a 18%Cr – 3%C white cast iron (after W.L. Guessser [21]).

Adding niobium to a white cast iron alloy has several metallurgical effects and consequences. Since niobium is a very strong carbide former, the amount of  $M_7C_3$  species is being reduced with increasing niobium addition to the alloy, (Figure 23) [22]. The replacement of  $M_7C_3$  by the harder NbC is noticed in an increased macro hardness of alloys with niobium addition. Furthermore, the formation of NbC also has an influence on the matrix metallurgy. NbC binds more carbon than  $M_7C_3$ , hence the matrix is more carbon depleted. The consequence is a lower amount of retained austenite after heat treatment. This, together with the higher effectiveness of molybdenum in the presence of niobium, results in an increased matrix hardness. The macro hardness reflects a combination of the harder matrix, as well as the harder NbC fraction. On the other hand, the reduced volume fraction of  $M_7C_3$  leaves a higher content of free chromium in the matrix, being beneficial for hardenability and corrosion resistance.

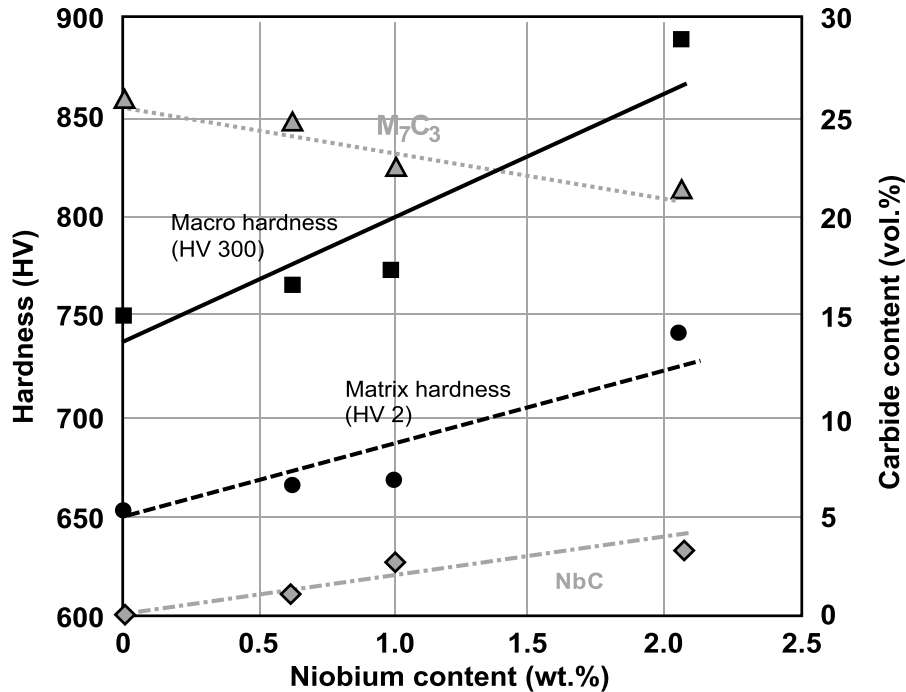


Figure 23. Macro (HV 300) and matrix micro-hardness (HV 2), and carbide content, versus niobium addition for a 2.94%C, 16.7%Cr, 0.83%Mo and 0.72%Cu iron (heat treated) [22].

The high chromium (11-30%) and carbon (1.8-3.6%) contents in high-Cr white cast iron generate an as-cast microstructure of hard eutectic  $M_7C_3$  type carbides in an austenitic matrix [23]. Hypereutectic high chromium cast irons are often the preferred alloys for hard facing and ultra-high wear applications. Their excellent abrasion resistance is based on the high volume fraction of hard (1300-1800 HV)  $Cr_7C_3$  carbides in the microstructure. The as-cast austenitic matrix is often destabilized by heat treatment to form a mixture of martensite/austenite with small precipitated secondary carbides within the prior austenite dendrites providing maximum hardness in the system [24]. During solidification,  $Cr_7C_3$  carbides grow as rods and blades with their long axes parallel to the heat flow direction in the mold. The carbides can reach a size in the order of 0.5 mm [25] and are interconnected throughout the microstructure, providing an easy and low energy path for crack propagation [26]. Accordingly, such microstructures tend to have low fracture toughness.

Consequently, the research trend in high wear resistant cast irons has been to control the shape, size, interconnection, volume fraction and distribution of hard particles by modifying the alloy design or changing the processing metallurgy.

Previous work was performed in order to control the structure of alloy white cast irons [24,25,27-35]. Increasing the cooling rate during conventional casting can reduce the carbide size, but this process modification is limited by the section thickness, being effective only for sections thinner than 50 mm. Therefore, it is not applicable for manufacturing larger components. Hanlon et al. [25] characterized the spray forming process of alloy WCI, achieving one order of magnitude reduction in carbide size. This technique considerably improves the wear resistance. However, the spray forming process substantially increases the production cost.

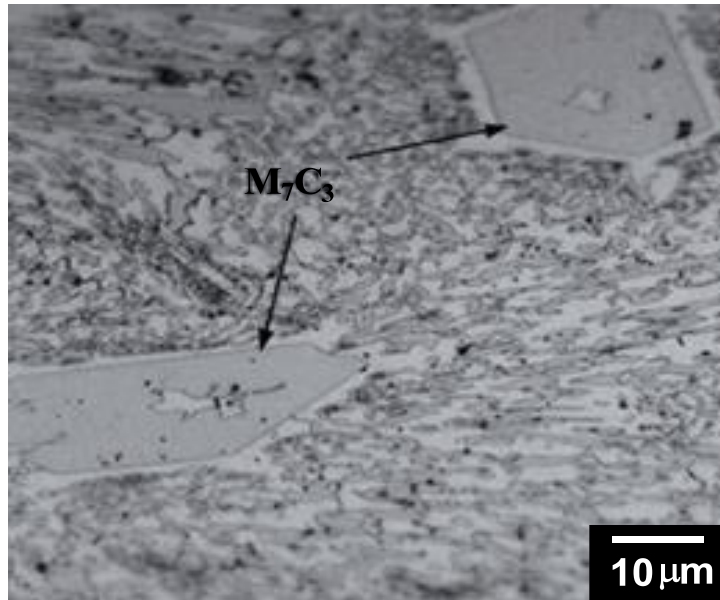
Various attempts of alloy chemistry modification have been done as well. Boron was added to a 13%Cr iron [27] and to a 28%Cr iron [28] generating changes in the carbide morphology from interconnected, coarse and clustered rods to a parallel distribution of isolated and fine rods. Rare earth elements have been successfully used to modify the carbide structure of low chromium white irons [29-32]. However, the rare earth elements showed no apparent effect on the morphology of the  $M_7C_3$  type carbides of high-Cr WCI [31]. Powell and Randle [33] observed a reduction in the carbide interconnectivity with the addition of 1.3% silicon to 18%Cr iron. Laird and Powell [24] affirmed that silicon inhibits the nucleation of the  $M_7C_3$  carbides in 18%Cr iron, while on the other hand, Shen and Zhou [34] reported an increase in carbide phase nucleation due to similar silicon additions.

Carbide forming elements, such as niobium, titanium, vanadium, tungsten, hafnium, tantalum and zirconium were also added (from 0.10 up to 7.0 wt.%) to WCI castings, WCI-based hard-facing overlay and also high speed steels. All sources and authors converge to the same conclusion, considering that the presence of such elements significantly affects the mechanical properties by influencing the structure of the hard phases (hard particles) and also enhancing the strength of the matrix. The changes in the hard phases generate an improvement of the tribological properties by changing the chemical composition and dispersion of these particles throughout the microstructure [37-40].

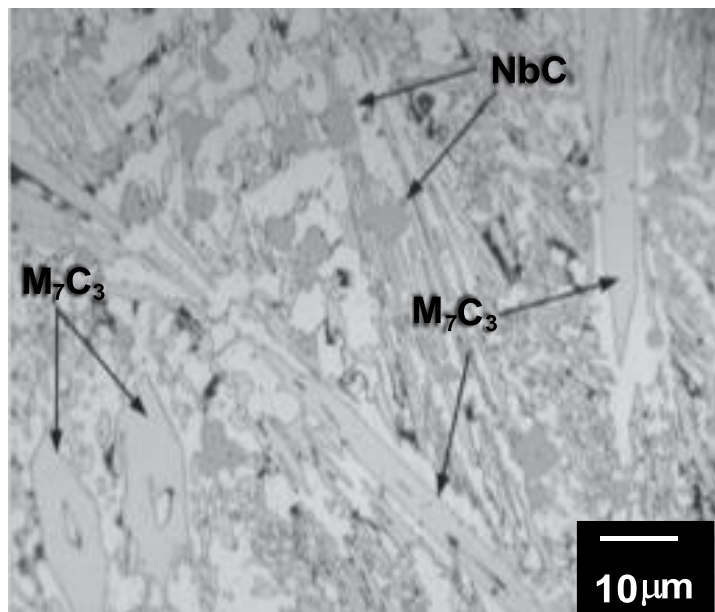
Hence, it is clear that the control of the hard particles goes beyond just basic carbide morphology by altering the growth mechanism; it can be done by enhancing the nucleation rate via innovative alloying techniques that promotes the formation of primary carbides that would not only hinder the growth of  $Cr_7C_3$  and boost the toughness, but also act as harder particles to improve even further the wear resistance.

#### Experience with NbC Reinforced White Cast Iron

Hard facing overlay is an application that is currently already using niobium additions to enhance the wear resistance. Commercial grades of WCI based hard facing overlay consumables include CORODUR 60TM, AI 1543TM and HARDFACE CN-O/S/GTM. These consumables have a basic chemistry of 5.5%C, 22%Cr, 1%Si and 7%Nb by adding a mechanical mixture of ferroalloys (FeNb, HCFeCr and FeSi ground together) directly in the cored-wire, so the carbides are formed *in-situ* during the arcing time of the hard facing process. The result is an increased wear resistance due to the presence of NbC and the refining effect of the primary NbC. This technique is limited to 8.0 wt.% of niobium addition, because the arcing time is too short (5 to 10 seconds) leaving insufficient time for NbC to form and disperse homogeneously in the weld deposit. Figure 24 compares the effect of niobium addition on the microstructure and carbide morphology in a WCI hard facing layer.



27%Cr; 4.2%C; 0.5%Mn; 0.5%Si  
(30 vol.% hard particles)



22%Cr; 4.5%C; 0.5%Mn; 0.5%Si; 6.5%Nb  
(55 vol.% hard particles)

Figure 24. Size and morphology of carbides in high-Cr WCI without and with Nb addition [41].



An improved hard-facing consumable production method allows the addition of higher amounts of carbide forming elements [36] including niobium, resulting in the formation of a very homogeneous dispersion of hard particles in the as-cast microstructure. The idea is to produce a homogeneous melt with the required concentration of the key elements, being: Fe, C, Cr, and Nb. This homogeneous melt is being produced from solid raw materials (ie. steel scrap and/or WCI scrap, HCFer, FeNb, as well as a source of free carbon such as graphite). It must be held liquid sufficiently long to dissolve the carbon and homogenize the composition of the melt so as to produce the desired level of combined-carbon (carbides). After casting the heat in small ingots, a powder is produced from it by crushing and milling operations to fill the cored-wires for the defined hard-facing procedure. Additions up to 35 wt.%Nb were tested on laboratory and industrial scale with positive results. The wear resistance was significantly improved providing up to a 4-fold increase of service life in specific applications by adding 20 wt.%Nb. Figure 25 demonstrates a quite homogeneous distribution of compact NbC particles at a level of 15 vol.% in high-Cr white cast iron [41].

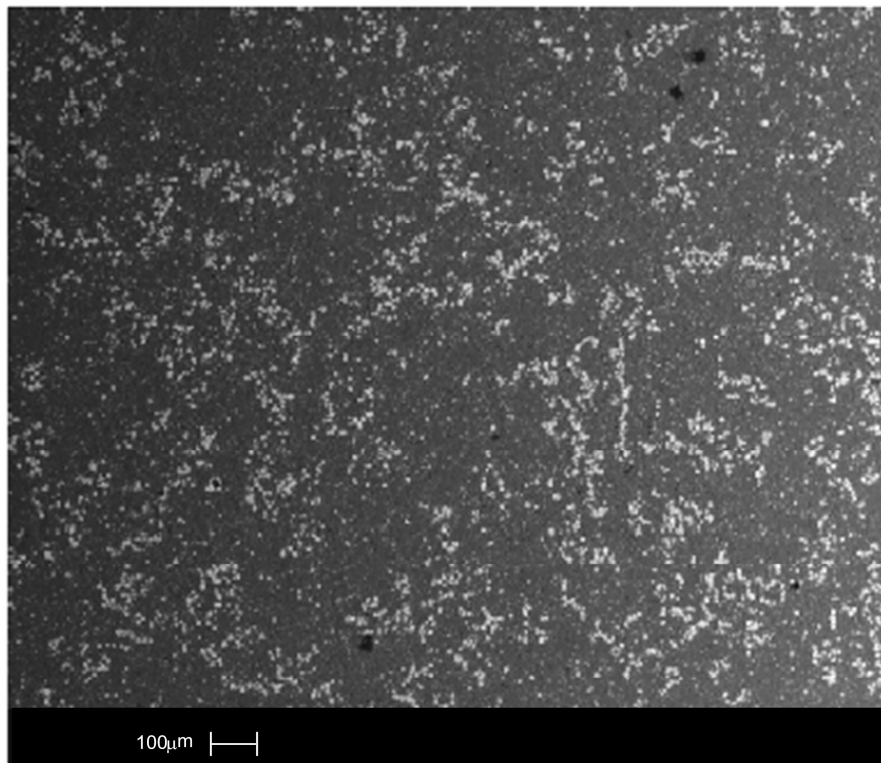


Figure 25. NbC particle distribution (bright contrast) in the microstructure of high-Cr WCI added with 15 wt.%NbC [41].

The same approach can be used for casting components. The wear resistance of high-Cr WCI castings can be greatly enhanced by macro-additions of niobium. An example of such a concept is the production of slurry pump impellers for the mining industry. A new alloy concept comprises WCI with up to 25 wt.%NbC, and the results show substantial improvement of the casting part service life [42]. A field trial with a slurry pump impeller made from white cast iron containing 15 wt.%NbC particles at CBMM's mining site in Araxá, Brazil revealed a 300% increase in the service life as compared to the NbC-free standard alloy, (Figure 26).

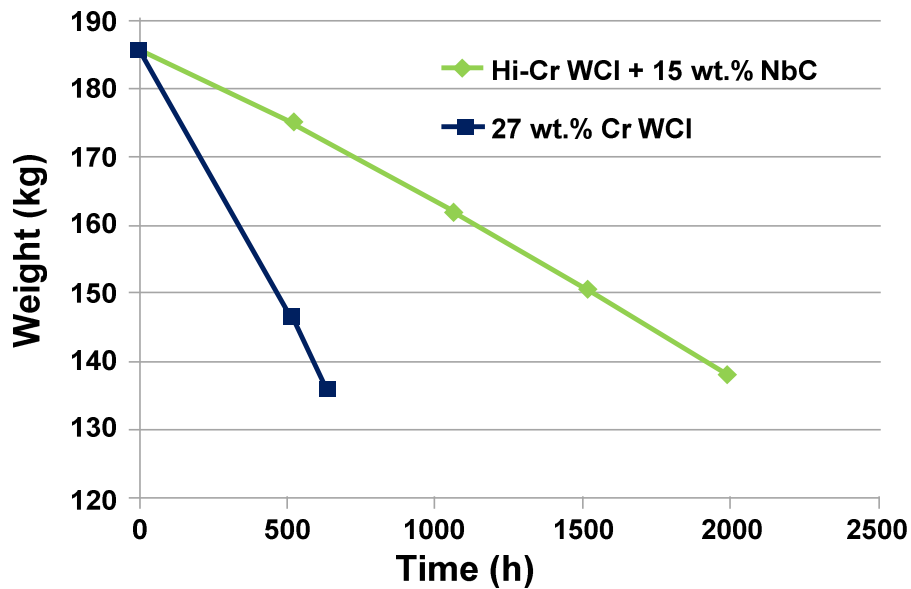


Figure 26. Field trial results demonstrating the service life increase of a slurry pump impeller at CBMM mine (Araxá, Brazil) due to the addition of 15 wt.%NbC to white cast iron (WCI).

### Conclusions

Molybdenum is an established and essential alloying element in many abrasion resistant iron and steel alloys. It increases hardenability most efficiently. This is particularly important when producing plate or cast components with large dimensions. Under particular processing conditions molybdenum also enables a TRIP effect by preserving retained austenite providing high work hardening during service. Molybdenum either by itself or in combination with other alloying elements forms hard carbide particles that are dispersed in the steel matrix. Such hard carbide precipitates further contribute to wear resistance. Combined alloying of molybdenum and niobium enables synergies such as a more efficient prior austenite grain size control and increased tempering resistance.

Niobium has been introduced more recently as an alloying element in abrasion resistant alloys. Micro additions of niobium to abrasion resistant steel refine the microstructure and mainly increase toughness. Larger additions of niobium can produce either primary or eutectic carbide particles. NbC particles are extremely hard and significantly enhance wear resistance. The formation of macroscopic NbC particles also reduces the amount of other transition metal carbides. Accordingly, a larger proportion of molybdenum and chromium stay in solution, contributing to increased hardenability and corrosion resistance.

Friction and wear properties of pure NbC have been recently investigated in detail for the first time. The results indicate a very high tribological performance of NbC in contact against metallic and ceramic materials [43].

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