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Niobium in Cast Irons

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<http://dx.doi.org/10.5772/64498>

Abstract

This work reviews the effect of niobium on different cast irons. This alloying element has a high affinity by carbon forming carbides of the type MC; therefore, the main effect is to strengthen the matrix of the alloys due to a hard-phase dispersion mechanism. Even at low levels of niobium ($<0.2\%$), MC carbides are found. The presence of such carbides increases hardness, yield and tensile strength in ductile irons, but the most important role is to increase wear resistance. Therefore, the use of niobium has been focussed mainly in alloyed white irons for wear resistance applications and in mottled cast iron used for rolls in hot rolling mills.

Keywords: cast iron, niobium, carbides, wear

1. Introduction

1.1. Cast irons

Cast irons are ferrous alloys containing carbon contents generally between 2 and 4 wt.%. Ferrous alloys with carbon contents below 2 wt.% are called steels. The high amount of carbon in cast irons exceeds the solubility of this element in ferrite and/or austenite; the excess of carbon promotes the precipitation of a carbon rich phase during solidification, which remains during cooling to room temperature. This phase can be a carbide or graphite. Therefore, the final structure of cast irons is composed by a metallic matrix and carbide or graphite, depending on the chemical composition and on the solidification rate. According to the microstructure, cast irons are classified as white, grey, ductile and mottled irons.

1.1.1. White iron

Without alloying elements, a Fe-C alloy solidifies mostly as a eutectic austenite–cementite (γ -Fe₃C). During cooling, austenite transforms to pearlite and the carbide remains. Thus, the typical structure is a continuous network of the brittle cementite containing islands of pearlite as shown from **Figure 1**. This structure makes this material too brittle and practically not useful for engineering applications.

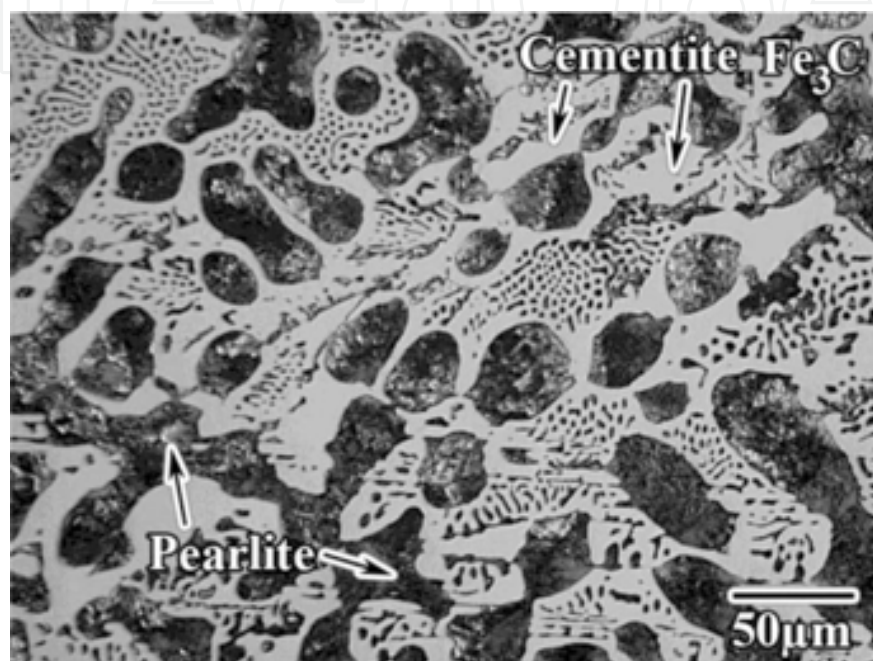


Figure 1. Typical structure of unalloyed white iron consisting of a network of cementite and pearlite.

1.1.2. Alloyed white iron

Since the continuous network of cementite promotes brittleness in white iron, it is common to alloy such materials to get better mechanical properties. A very successful element for this purpose is chromium. In amounts between 12 and 30wt.%, chromium changes the stoichiometry of the carbide phase from the orthorhombic M₃C to the hexagonal M₇C₃, which is less continuous. In addition, the presence of other elements such as nickel and molybdenum, which increase hardenability, promotes the presence of the austenite in the final as-cast structure. These irons are called high-chromium cast irons, and the as-cast structure consists of eutectic carbides of the type M₇C₃ in a matrix of austenite (**Figure 2**). The presence of austenite and the less interconnected carbides gives some toughness to the alloy, and the harder M₇C₃ carbide gives a better wear resistance to these materials.

If the amount of chromium is less than 12wt.%, the stoichiometry of the carbide does not change and the structure consists of eutectic M₃C carbides in a matrix of austenite plus martensite. These irons are called low-chromium cast irons. **Figure 3** shows the typical as-cast structure of this latter iron.

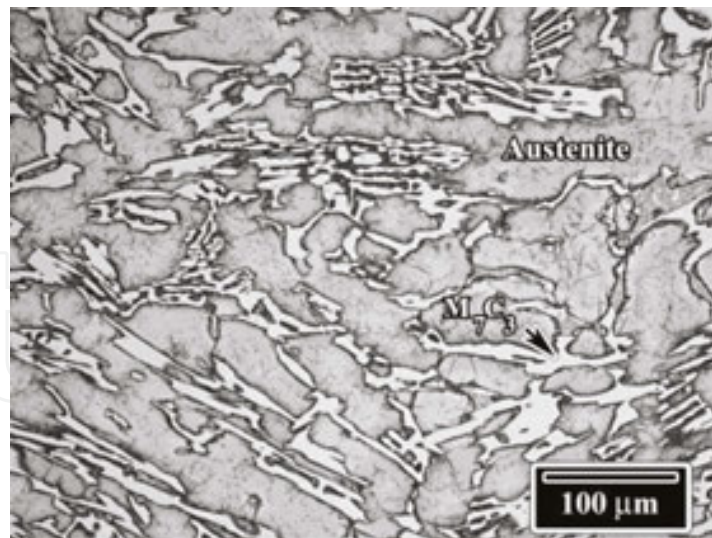


Figure 2. Typical as-cast microstructure of a high-chromium white iron consisting of eutectic M_7C_3 carbides in a matrix of austenite.

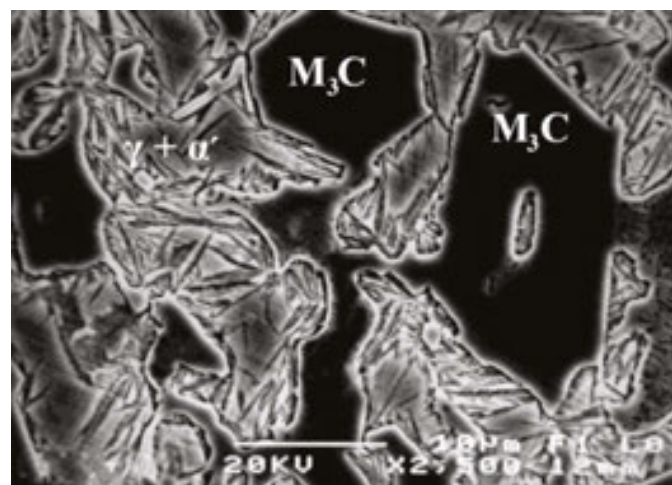


Figure 3. Typical as-cast microstructure of a low-chromium white iron consisting of eutectic M_3C carbides in a matrix of austenite (γ) plus martensite (α').

1.1.3. Grey iron

Without carbide-forming elements and the presence of silicon in cast irons, the carbon excess precipitates as graphite instead of carbide during solidification. Under these circumstances, the as-cast structure is composed by graphite “flakes” in a mainly pearlitic matrix. **Figure 4** shows the as-polished (a) and as-etched (b) structure of a 2%Si 3%C grey iron. **Figure 5** shows the tridimensional “flake-like” morphology of graphite at the fractured surface of the iron shown in **Figure 4**. One of the main characteristics of grey iron is the size, type and distribution of graphite according to the ASTM A247 standard [1]. Such characteristics depend on the solidification rate and on the effectiveness of the inoculation process before pouring.

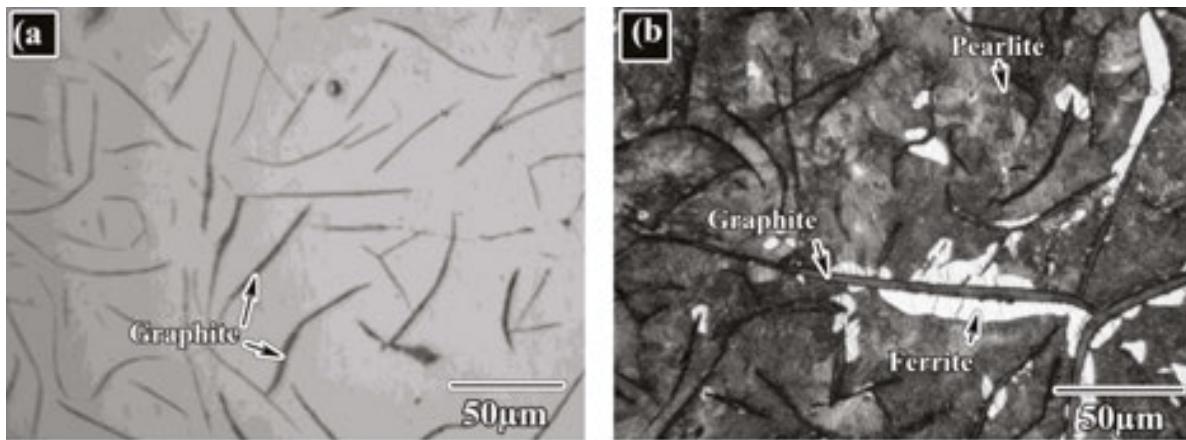


Figure 4. Microstructure of grey iron (a) as-polished, showing the flake-like graphite, and (b) 2% nital etched, showing the matrix to be composed by pearlite and small amounts of ferrite.

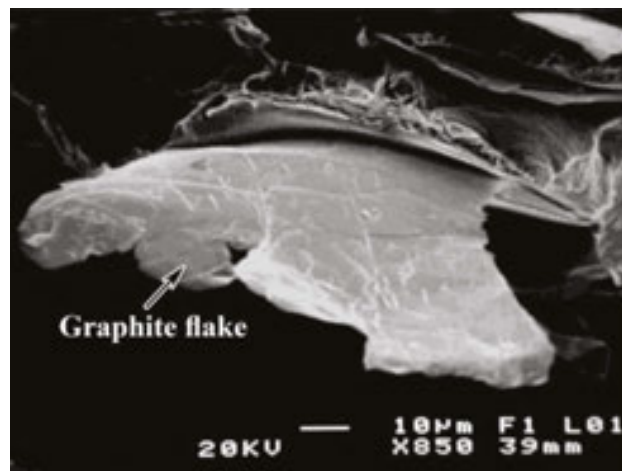


Figure 5. Tridimensional morphology of a graphite flake in a grey cast iron.

1.1.4. Ductile iron

Ductile iron has the same chemical composition than grey iron; the difference is a particular treatment with small amounts of magnesium or cerium which is applied to the liquid alloy. Such a treatment promotes the excess of carbon to precipitate as spheres during the eutectic solidification. Then, the microstructure is composed by a continuous matrix of pearlite plus ferrite and isolated spheres of graphite. The amount of ferrite and pearlite depends on the solidification rate, the alloying elements and on the effectiveness of the inoculants. The continuous matrix increases mechanical properties and makes these irons comparable with some steels. **Figure 6** shows the microstructure of two ductile cast irons evidencing the effect of copper on the amount of pearlite. The base chemical composition for both irons is 3.14%C, 2.5%Si and 0.5%Mn. It is common to find the ferrite phase surrounding the graphite spheres in ferritic/pearlitic ductile cast irons due to the solidification nature of the alloy.

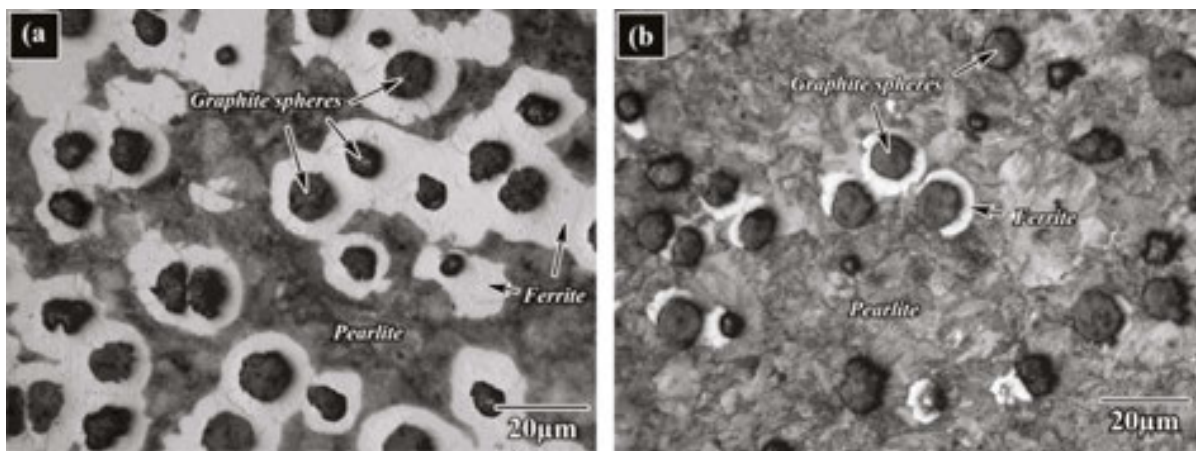


Figure 6. As-cast microstructure of ductile iron, (a) 3.14%C, 2.5%Si and 0.5%Mn showing a matrix composed of 50% ferrite-50% pearlite; (b) the same base composition of (a) but with the addition of 0.2%Cu, showing a matrix composed of 90% pearlite and 10% ferrite.

1.1.5. Mottled iron

Mottled iron is a mixture of white and grey/ductile iron; the excess of carbon precipitates both as graphite and as carbide. The presence of carbide-forming elements (chromium, manganese, molybdenum, etc) is common in these irons in order to form the M_3C carbide; in addition, the presence of silicon and nickel is also necessary to promote the precipitation of graphite. If treated with magnesium, the graphite phase can be obtained as “spheres” as in ductile iron; other way, the graphite will be present as “flakes” as in grey iron.

Figure 7 shows two micrographs showing the typical structure of a mottled iron 3.2%C-0.52%Mn-2.24%Si-0.53%Cr-3.49%Ni-0.56%Mo-0.2%Cu. The iron was magnesium-treated to obtain nodules of graphite, and the main application of this alloy is for mill rolls [2].

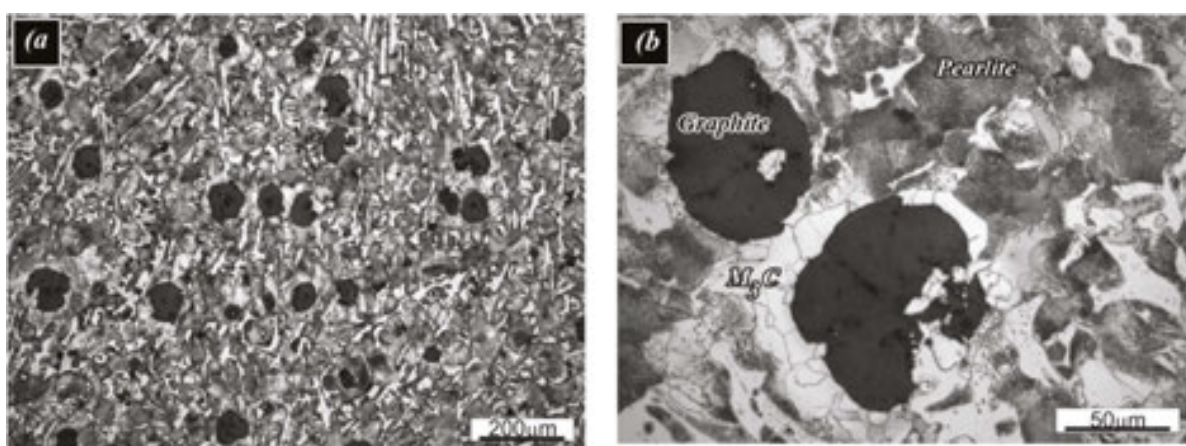


Figure 7. Microstructure of a mottled iron showing the microstructure to be composed by graphite nodules and M_3C carbides in a matrix of pearlite (micrographs kindly provided by Prof. Janus Krawczyk, from the AGH University of Science and Technology, Krakow, Poland).

1.2. Niobium properties and applications

According to Takai [3], the discovery of niobium can be attributed to two people; first of all, to an English chemist named C. Hatchett, the first name that was given to this new element was "*Columbium*" since Columbia was the place where it was discovered. Secondly, by the year 1844, H. Rose, a German chemist, managed to separate a new element from tantalum and named it "*Niobium*". Two years later, it was proven and worldwide recognised that both elements were the same. The International Union of Chemistry Congress adopted the name niobium for the new element, which is the principal name used around the world; the name Columbium is used just in the USA. Niobium always coexists with tantalum in tantalite, the ore which is the main raw material for extracting tantalum.

Niobium is a refractory metal, such as tantalum, tungsten and molybdenum, and has a high melting point ($2468 \pm 10^\circ\text{C}$), being chemically stable against acid and alkali. Its physical properties, such as superconduction, low thermal neutron capture cross section, low corrosion under some environments, make this element an attractive candidate for so many applications in the fields of nuclear industry [3, 4], superconducting [5–7], acoustics and electro-optics [8], in biomedical devices [9], and other extreme applications as in corrosive environments [10] and cemented carbides [11].

Due to its soft magnetic properties and its ability to form glassy alloys [12], niobium has been also used in several alloys for magnets either cast [13, 14] or bond [15]. In addition, the chemistry of niobium is appropriate to form intermetallic compounds with iron such as FeNb, Fe₂Nb₃ depending on the content of other alloying elements [16, 17].

However, the main use of niobium as alloying element has been in iron alloys such as steels and cast irons. In the case of steels, the development of high-strength low-alloy steels more than 40 years ago, the use of niobium as a microalloying element was widely exploited. The role of niobium (in amounts $<0.1\%$) in refining the grain size of steels during the controlled thermomechanical processing has been deeply studied since then. It is well known that when dissolved in austenite retards recovery in hot deformed steels and avoids the deformation-induced ferrite transformation [18, 19] and also retards the static and dynamic recrystallisation [20]. One of the most important phenomena about niobium in steels is the strain-induced precipitation of NbC or NbCN during the thermomechanical processing [21–25]. The precipitation of such nanometric particles delays the grain growth during hot deformation, and more refined structures are obtained as a result of niobium microalloying and this in turn represents an increase in strength [26].

The ability of niobium compounds to precipitate during heat treatments has also been used as a tool for increasing the strength of some iron alloys, for example the precipitation of niobium compounds in HP heat-resistant cast stainless steels for creep applications [27] and the dispersion hardening in aged steels [28]. Furthermore, it has been observed that niobium additions modify the cast structure of niobium alloyed hot work tool steels and reduces the size and volume of eutectic cells and increases the maximum hardness of the steel [29].

1.3. Cast iron production

Cast iron is usually melted in a cupola furnace, an electric arc furnace, an induction electric furnace or an air (reverberatory) furnace. When melting in a cupola, the charge is composed of coke, steel scrap and pig iron in alternate layers of metal and coke. Sufficient limestone is added to flux the ash from the coke and from the slag. The amount of coke depends on the amount of carbon of the metallic charge (or the melting point); during melting, the coke burns as air is introduced through the furnace tuyeres and the metallic charge absorbs carbon from the coke. The amount of some other elements in the metallic charge are modified due to the oxidation process, for example, some manganese and silicon are oxidised and also some manganese combines with sulphur forming MnS, and the product of these reactions is incorporated to the slag [30]. A clear disadvantage of melting in a cupola is the oxidation reaction of carbon whose CO₂ emissions are not environmentally acceptable.

When melting in electric furnaces, the process is cleaner since no coke is added to the charge. When the metallic charge is melted, the chemical composition is adjusted by adding the proper amounts of ferroalloys according to the desired composition. The metallic charge may be high-carbon steel scrap or pig iron (see **Figure 8**).

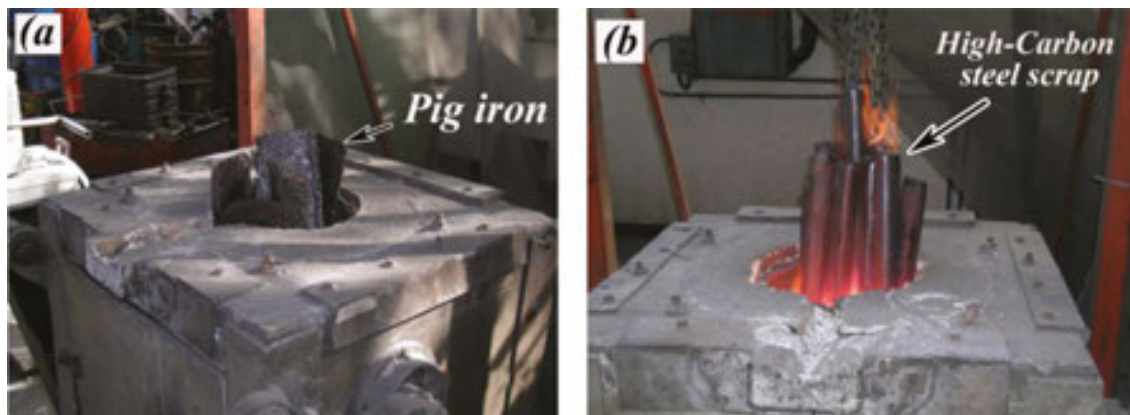


Figure 8. Induction furnace charged to produce cast iron, (a) when using pig iron as raw material and (b) when using steel scrap.

Once melted the metallic charge, the slag is mechanically removed to clean the surface in order to add the alloying elements. Under these conditions, the incorporating efficiency of such elements into the melt is higher. It is recommended to add the alloying elements as ferroalloys (ferro-manganese, ferro-silicon, ferro-niobium, etc), since their melting points are relatively low and this facilitates their dissolution in the liquid metal. Working temperatures of about 1500°C are common in many foundries since this allows to transport and treat the liquid metal before pouring it. Most of the alloying elements are added into the furnace; however, some others highly oxidised are added late in the ladle or even in the furnace but just before pouring into the ladle. In the particular case of niobium, it has a high affinity for carbon forming carbides even at very low levels of niobium. Such carbides of high melting point may be the first to solidify (depending on the carbon content of the alloy) and segregate in the liquid or even

incorporate to the slag; thus, the recovery of this element may be too low. Due to this, ferro-niobium injection techniques have been developed to increase the recovery of niobium in the solidified castings [31].

Once the chemical composition has been adjusted, the liquid metal is commonly poured into a ladle (**Figure 9**), where the inoculation process takes place (in the case of grey and ductile iron) or it is nodulised (magnesium treated in the case of ductile iron; **Figure 10**). Finally, when the melt has been already treated, it is commonly poured into sand moulds (**Figure 11**) for a slow solidification rate. Once solidified, the castings are extracted from the moulds by destroying them. Details of different iron production practices are found elsewhere [32].



Figure 9. Pouring the liquid iron into the preheated ladle in the ductile iron making.



Figure 10. Nodulising ductile iron with magnesium, note the intensity of the reaction when magnesium is added into the liquid metal.



Figure 11. Pouring the liquid iron into sand moulds.

2. Niobium effect on the structure and properties of cast irons

2.1. Niobium in grey iron

The use of niobium in steels has a long tradition; in most of the cases, it is restringed as a microalloying element ($<0.1\%$). Its use in cast irons is not as wide as in steels, and one of the main applications is in castings for making grey iron castings for the automotive industry. Grey cast iron has a very low ability to bend and low ductility, due to the presence of graphite flakes which act as discontinuities, but it has a low pouring temperature, high fluidity, low liquid to solid shrinkage, etc., that make it suitable for casting.

With the correct chemical composition, grey iron may be used for engine blocks and cylinder heads due to its excellent properties of thermal fatigue, while other chemical composition may improve its thermal conductivity and specific heat and may be used for disk brake rotors.

According to James et al. [33], the new performance requirements and more stringent automotive standards, engines are required to run hotter and at higher pressures. These requirements demand increase in strength and enhanced thermal fatigue resistance of grey iron castings, particularly in engine cylinder heads due to their proximity to the combustion chamber. During combustion, temperature in the chamber may be increased to 700°C and pressure as high as 160 MPa. This heat may be conducted to the cylinder head which may be cooled by circulating a coolant through channels therein. This cycling heating and cooling combined with the mechanical stresses due to the pressure on the cylinder wall make the cylinder head highly susceptible to thermal fatigue and creep. These properties may be enhanced by alloying elements in the grey cast iron.

Molybdenum and vanadium have been traditionally used in grey cast iron to increase thermal fatigue resistance. However, the use of niobium has been also investigated with some success [33]. This element has been added as a partial substitute of molybdenum (a more expensive element) and may be present in the alloy from 0.05 to 0.3% by weight. Very small amounts of carbides may be present in the structure and the main matrix is pearlite (**Figure 12**) although bainite and martensite may be present in small amounts. The strength of this as-cast alloy may be as high as 360 MPa. Other patented work [34] reports the use of niobium in amounts of 0.38 to 0.45% and the formation of fine carbides well dispersed and embedded in a pearlitic matrix which reduce wear during braking operations.

The replacement of molybdenum with niobium has also been studied in similar grey irons for brake disks but focussed on the effect of this alloying element in the low cycle fatigue [35]. According to the results, the fatigue behaviour of the alloy is improved when increasing the amount of niobium and decreasing molybdenum. They conclude that niobium can be replaced by molybdenum for this particular application and suggest to replace 0.32%Mo with 0.1%Nb. This benefit is attributed to the ability of niobium to refine the eutectic cells and graphite type, to the pearlite refinement (**Figure 13**) and to the precipitation of small niobium carbides that increase wear behaviour. In addition, the cost of the alloy is reduced.

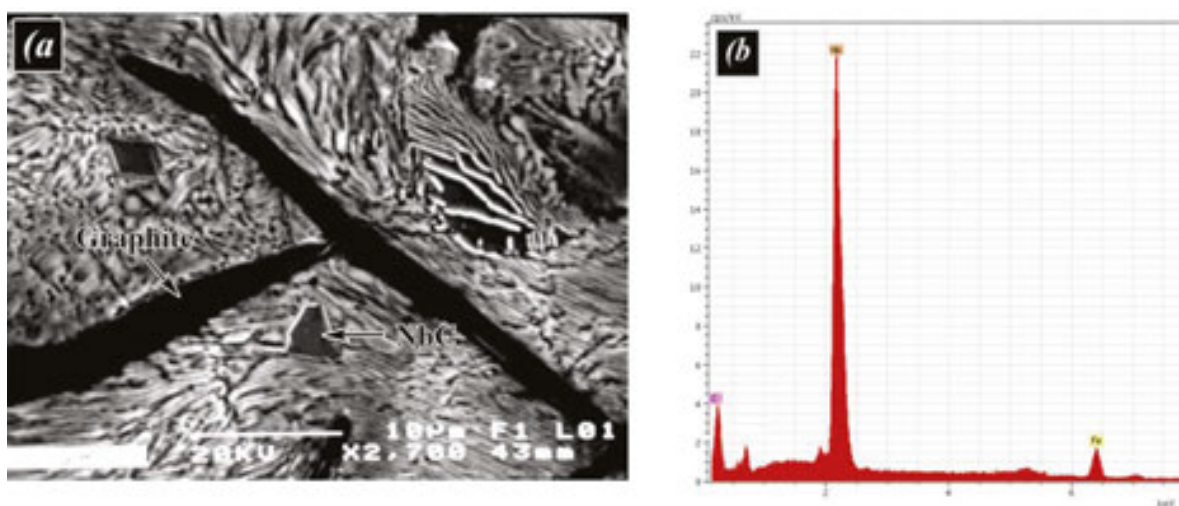


Figure 12. (a) Microstructure of 0.48%Nb grey cast iron showing a mainly pearlitic matrix and (b) EDS of the carbide particle arrowed in (a).

General aspects on the use of niobium in grey irons indicate amounts lower than 0.5% due to its high affinity for carbon. With this amounts, Nylen [36] highlights that the effect of this alloying element is a higher stability of austenite, an increase in microhardness, a small refinement of the graphite structure and the precipitation of small carbides. These microstructural features contribute to increase the tensile strength in the as-cast conditions from 205 MPa for an iron without niobium, to 270 MPa for an iron with 0.8%Nb.

Similar results have been also observed when adding up to 1.48%Nb in high-carbon equivalent cast irons for brake disks [37]. After a clear refinement of the graphite phase, the authors argue

that some niobium carbide particles may act as heterogeneous nucleation for graphite in the eutectic reaction. As a result, the increase in the nucleation rate produced a refined graphite morphology. Also, the pearlite lamellar spacing is reduced and it is attributed to the decrease in the eutectic temperature with the niobium additions. These microstructural features contribute in turn to increase hardness and wear resistance of the alloy after the addition of niobium.

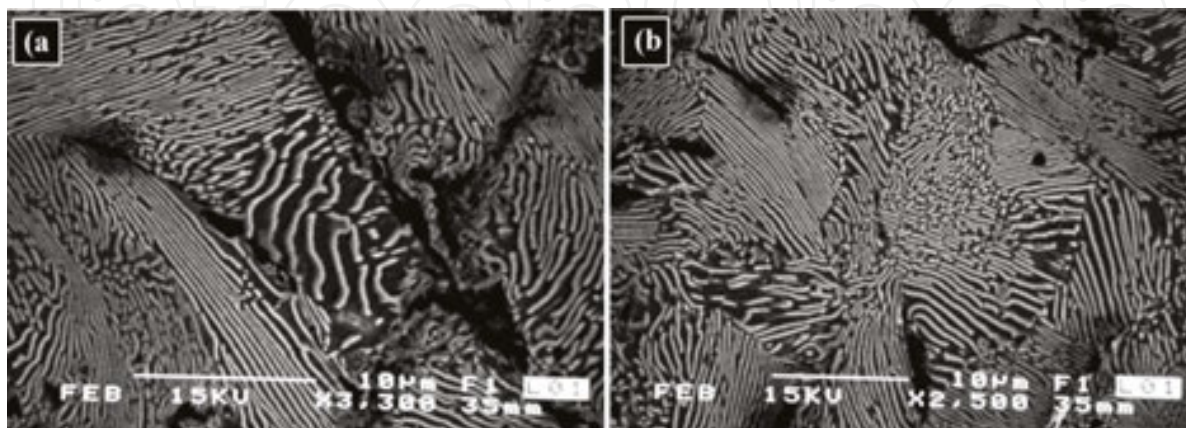


Figure 13. Refinement of the pearlite structure by the niobium addition. (a) Grey cast iron without niobium and (b) 0.32%Nb grey cast iron.

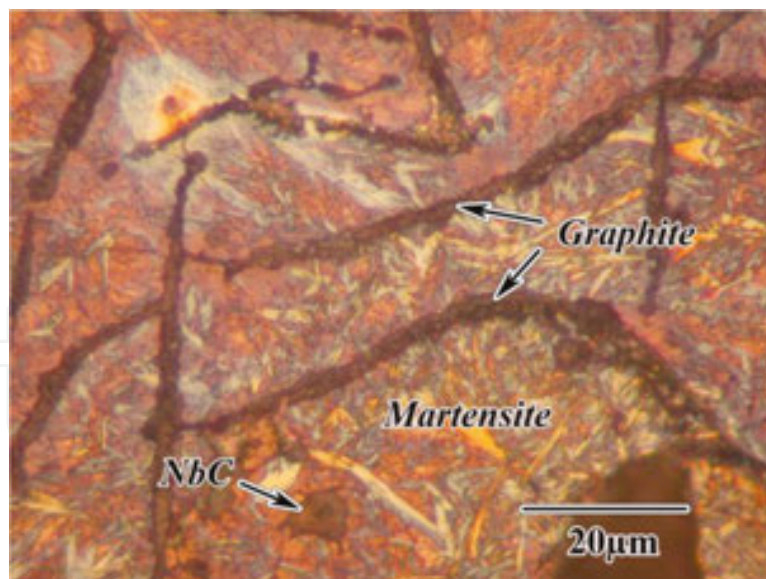


Figure 14. Martensitic matrix in a quenched and tempered grey iron containing 0.32%Nb.

The effect of niobium on strength and wear resistance of grey irons is noted only in the as-cast conditions, since when the alloy is quenched and tempered or austempered, the effect of niobium is minimised by the transformed matrix. This has been observed for high-carbon equivalent [38] and for hypereutectic grey irons [39]. The martensitic matrix (**Figure 14**) in the

quenched and tempered conditions increases strength and wear resistance. In the case of the austempered alloy, the ausferritic structure with 20% of retained austenite enhances the wear resistance through a strain-induced martensite transformation effect when the alloy is under frictional contact. The presence of niobium carbides prevents the loss of material during sliding by reinforcing the matrix and graphite serves as a lubricant lowering friction. However, when a carbide particle is released from the matrix, three-body abrasion may take place [40]. Similar results have been observed if the alloying element is titanium [41].

Grey iron has been also used as a base material for making NbC particulate reinforced iron matrix composites produced in situ [42]. The technique is to mixture grey iron powders with niobium wires of 0.7 mm diameter. After about 25 min at 1172°C, the niobium wires dissolved completely and combine with carbon of the alloy producing small well-distributed niobium carbides in an iron matrix.

2.2. Niobium in ductile iron

As mentioned above, the addition of niobium to liquid cast iron whose carbon content is high, which promotes the primary precipitation of solid niobium carbides before the rest of the alloy starts solidifying. Such precipitation may produce segregation and agglomeration of such particles, and it is also common to eliminate them if they get incorporated to the slag. Then, niobium additions must be done at later stages of the melting process [36].

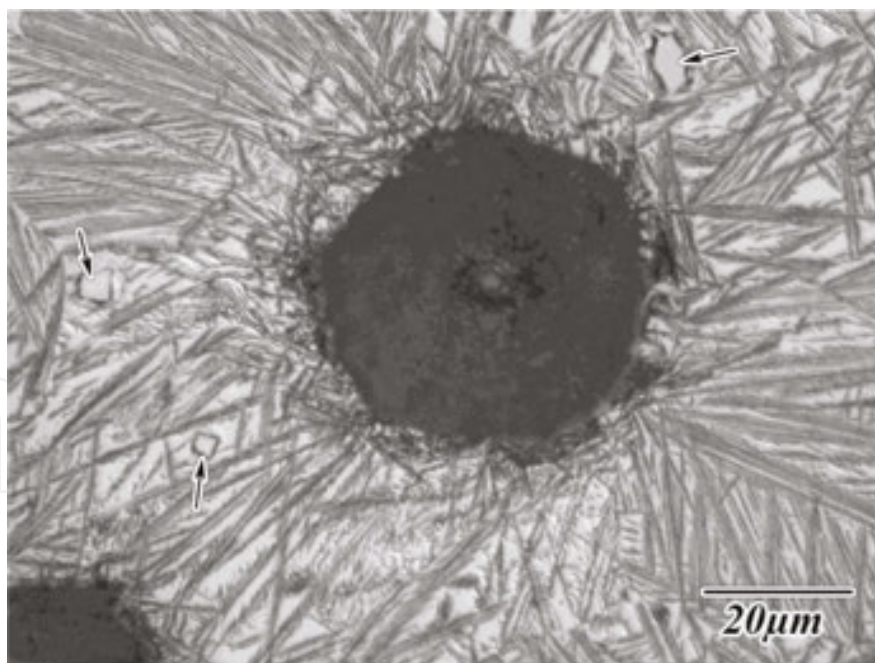


Figure 15. Austempered ductile iron with 0.3%Nb. Note the presence of NbC (arrowed) in the ausferritic structure.

Ductile iron is almost always made for applications where some toughness or ductility is required, and the presence of massive carbides is considered as a detrimental feature for this particular alloy. An increase in strength is generally associated with a decrease in ductility or

toughness in an alloy. This is particularly true in ductile irons; it is always desirable to increase strength and retain a good ductility. This has led to the development of heat treatments to obtain high strength in ductile irons as well as good ductility. A particular heat treatment is the “austempering” and the heat-treated irons are called “*austempered ductile irons*” (ADI) [43]. The acicular structure obtained by this heat treatment provides high strength but low ductilities (usually below 5%). **Figure 15** shows the ausferritic structure typical of ADI; in this case, it is a ductile iron with 0.3%Nb. Note the presence of the NbC (arrowed) particles in the structure. This structure of the matrix minimises the effect of niobium in strength and wear resistance of the iron and also its effect on fatigue properties [44].

However, heat treatment always implies higher production costs and is time-consuming. Therefore, it is preferable to obtain the desirable mechanical properties for the alloy in the as-cast conditions by controlling the solidification process and/or chemical composition.

The election of heat treatments or chemical additions is a particular decision of each foundry according to a balance of production costs. In some countries, the addition of a particular alloying element may be cheaper than undertaking a heat treatment, whereas in others to undertake a heat treatment is preferable. When chemical addition is the preferred production practice, the addition of a single element may contribute to a significant refinement of the pearlite constituent, particularly when such element dissolves in austenite, favouring hardenability.

The influence of alloying elements on the mechanical properties of ductile iron is related to the effect of such elements on the ferrite and pearlite contents in the matrix. Alloying elements may increase the strength of ferrite by solid solution strengthening and also of pearlite by reducing the interlamellar spacing. They may also affect the relative amount of pearlite and ferrite as a result of their effect on the eutectoid temperature and transformation kinetics. The strengthening obtained by alloying depends on the type of matrix since the strengthening mechanisms in pearlite and ferrite are not the same. In irons with mixed ferrite–pearlite matrices, the strengthening level depends on the relative amounts of ferrite and pearlite.

The addition of considerable amounts of nickel (4%) and molybdenum (0.5%) is a common practice to produce high resistance ductile irons in the as-cast conditions due to the bainitic matrix produced by these chemical combinations. Such a matrix is obtained due to the excellent synergism of these elements in improving hardenability, as mentioned above. However, the production cost may be high since these are very expensive elements in most of the countries.

It has been reported by Kawamoto et al. [45] that the addition of carbide-forming elements (Mo, V and Ti) to ductile iron affects mechanical properties by influencing the strength of the matrix and the composition and dispersion of the carbide phase. Niobium is known to form an extremely hard MC type carbide.

Niobium has been added to refine austenite grain size during solidification. This phenomenon has been observed to take place owing to niobium carbide formation which retards austenite grain growth. These carbides form at high temperatures and may serve as nuclei for the proeutectic austenite precipitation and perhaps for the eutectic colonies as well. Niobium increases the volume fraction of eutectic austenite as this element reduces the carbon amount

precipitating as graphite during eutectic solidification. However, the effect of some other elements in the alloy also alters the eutectic carbon content (silicon and phosphorous), causing a change in the amount of proeutectic austenite.

Niobium in ductile irons has been reported to be found as NbC which forms during the first stage of solidification, during proeutectic austenite formation and before the eutectic reaction [46]. In a particular research work [47], niobium additions up to 0.8% to a ductile iron, formed rectangular niobium carbides whose size and volume fraction increased as niobium content increased. Particles up to 4 μm size were found in irons with niobium additions below 0.4% and particles as large as 10 μm were observed for irons with 0.8%Nb (see **Figure 16**). The volume fraction of NbC was about 0.01 for this later amount of niobium. Niobium also contributed to an increase in the amount of pearlite in the matrix and a decrease in the graphite volume fraction. It is suggested that most of the niobium content combines to form NbC, but a small amount must be dissolved in matrix contributing to the increase in pearlite formation. The increase in pearlite was reported from 70 to 77% when the niobium amount was 0.8%. Regarding to the graphite volume fraction, it decreased from 12 to 8% for the 0.8%Nb. Since niobium carbides form before eutectic solidification, they consume some of the available carbon for graphite nodules; therefore, the volume of graphite after eutectic solidification was observed to diminish. This effect of niobium in the microstructure contributed to a small increase in yield (from 650 to 722 MPa) and tensile strength (from 866 to 930 MPa) and hardness (from 27 to 33 HRC) along with a decrease in ductility (from 12 to 5%).

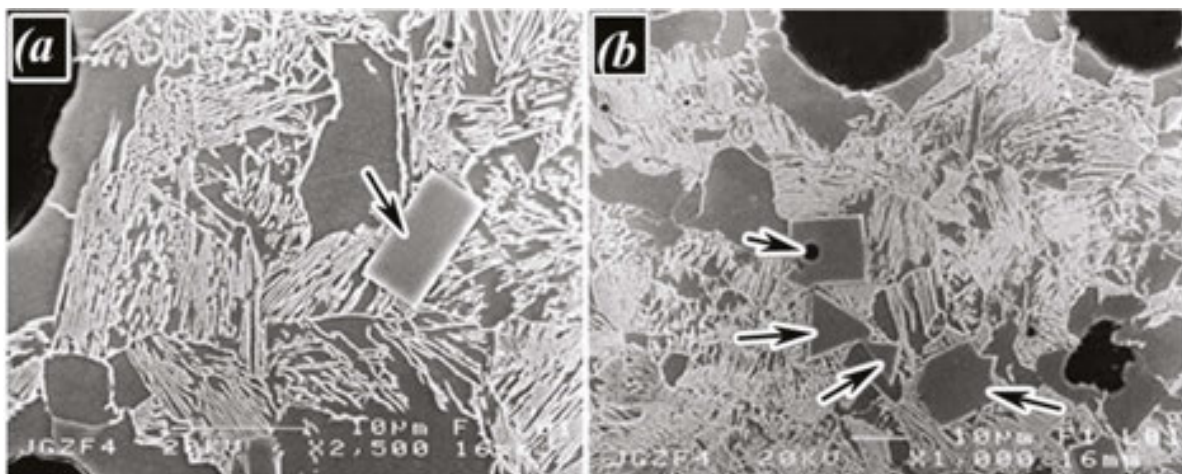


Figure 16. As-cast ductile irons (a) 0.4%Nb and (b) 0.8%Nb. Note the presence of NbC (arrowed).

2.3. Niobium in mottled iron

The main application for mottled irons with nodular graphite is for rolls in hot rolling and in other wear-resistant applications. They contain both graphite and carbide (Fe_3C or M_3C depending of the alloying elements). The presence of carbide and graphite ensures good enough wear resistance. According to Nysten [36], there are two strategies to improve wear performance for this kind of irons: (i) increase the overall hardness by increasing the proportion

of cementite, but the alloy becomes more sensitive to crack and (ii) increase the total amount of carbides but with the risk to offset the graphite/carbide balance. The combination of graphite and carbide gives to the alloy other important properties for this iron: low adhesion to the trip and good thermal crack resistance as well as good elastic modulus [48, 49].

One of the strategies for improving the performance of these alloys has been focussed on the increase in the amount of the carbide phase. The AKERS group, in Sweden, has been working in the addition of a carbide-forming element to increase the carbide phase in mottled iron and other irons for rolling mills, niobium. However, the main difficulties of adding niobium to melt iron are the segregation of the particles during solidification, since these particles are the first to solidify. Under these conditions, it is difficult to obtain a good distribution of the NbC in the alloy. **Figure 17** shows the microstructure of a mottled cast iron with 1% Nb, note the agglomeration of NbC particles caused by segregation during solidification.

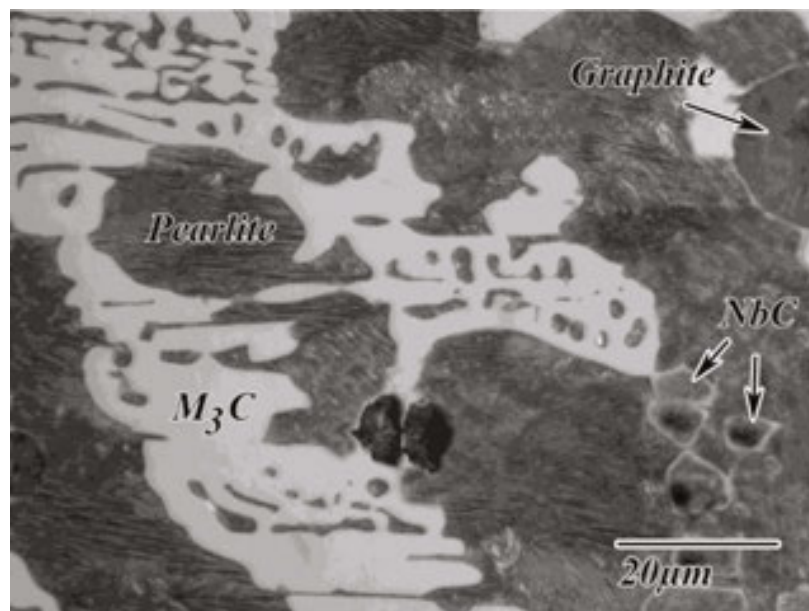


Figure 17. Mottled cast irons showing the segregation of NbC in the microstructure.

The purpose of Akers has been to develop a more wear-resistant material by adding carbide-forming elements without losing the favourable properties of the alloy. This should be done without upsetting the balance of carbide/graphite or to any major extent change the matrix composition of the base alloy. The presence of graphite in the alloy 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 and reduces the potential for welding of the trip to the roll.

In order to get the proper balance of graphite and carbides in these alloys, some requirements have been highlighted by Nylen [36], and these include as follows: (i) an extremely careful selection of melting raw materials, (ii) controlled melting conditions, (iii) adequate control of composition and (iv) efficient inoculation techniques to get the required type and distribution

of graphite. According to him, this correct balance may help to avoid the use of stronger carbide-forming elements, which can promote the formation of massive carbides within the structure of the iron. The Akers group has been working hard in these actions, and they conclude that the use of niobium in mottled irons has a massive potential future.

2.4. Niobium in white iron

Undoubtedly, the major amount of work on niobium additions to cast irons has been undertaken to white cast irons, since the main application for these alloys is in the field of the wear resistance, where the NbC particles play an important role.

Since the accidental discovery of the white cast iron by Robert Ransome, an agricultural machinery manufacturer in Ipswich, England, at the turn of the eighteenth century [50], the art of manufacturing this iron has slowly become a science. At the time of Ransome's discovery, it was known only that a harder, more wear-resistant iron was formed when iron was rapidly cooled. Furthermore, when this iron was fractured, the surface appeared white and, hence, the name white cast iron. Initial applications for this iron at that time were limited to thin sections since a high freezing rate was required for its manufacture. It was not until the first part of the twentieth century that the carbide-stabilising ability of chromium was fully recognised with the advent of a 25–30% chromium-alloyed white cast iron. This new alloy could be cast white into almost any section size and was significantly more wear resistant than unalloyed white cast iron. Lower chromium irons were subsequently introduced that were alloyed with nickel mainly for hardenability [51].

Since this discovery, so many researchers have gradually contributed to the knowledge of the metallurgy of cast iron and to establish the relationship between chemical alloying, processing routes and mechanical properties, as highlighted by Tabret et al. [52] in their interesting review. In addition, since nowadays white iron alloys are highly alloyed complex materials, they suggest that this complex chemistry demands a deep understanding of the metallurgy of cast irons during their production and processing. ASTM specification A532 [53] covers the composition of the abrasion-resistant white irons in use.

The ASTM standard classifies these alloys as abrasion-resistant because in the mining industry, which is the main user, such irons are used in a range of situations which are subject to varying conditions where the main wear mechanism is the abrasive one, that is crushing, screening, and pumping [52]. Furthermore, in the steel industry, Hi-Cr irons are widely used for rolls in hot rolling mills [54], where the mechanisms of damage are abrasion of the matrix and rolling contact fatigue [55, 56]. Such deterioration of the rolls surface causes strip surface flaw [57].

Hi-Cr white irons are based on the Fe-Cr-C ternary system. Jackson [58] was one of the first researchers to study systematically this alloy and its solidification sequence. Commercial Hi-Cr alloys often contain further alloying elements such as molybdenum, nickel, copper and manganese [52], which may modify the solidification behaviour and the amount of phases present in the alloy. For example, molybdenum additions contribute to increase hardenability and avoid pearlite formation; in such case, the analysis of a quaternary system is necessary as highlighted by Qiu [59]. However, chromium and carbon contents are the main parameters

describing the solidification path of the Hi-Cr irons and the ternary Fe-Cr-C system is used to describe the first stages of solidification on any commercial alloy of this type.

According to this, the common compositions go from 1.8 to 3.5%C and from 12 to 30%Cr. Under these conditions, the most common alloys are hypoeutectic and the solidification path is as follows: solidification starts with the formation of dendrites of primary austenite which grow and reject carbon towards the interdendritic regions; as the solidification progresses, temperature decreases and the remaining liquid gets richer in carbon until it reaches the eutectic composition. At this temperature, the eutectic reaction occurs

Although the austenite that forms on solidification is not stable at room temperature, a metastable austenitic matrix is commonly retained in the ambient temperature structure. More commonly, the M_s temperature is slightly above ambient temperature, while the martensite finish temperature, M_f , is below. This produces some transformation on cooling so that martensite may be present in the predominantly austenitic as-cast structure [52].

The as-cast microstructure of hypoeutectic Hi-Cr white irons typically consists of austenite dendrites (with possibly partial transformation to martensite, pearlite or bainite) and an interdendritic eutectic of carbides and partially transformed austenite. An example of the microstructure of a sand cast 17%Cr-2.6%C-2%Ni-2%Mo is given in **Figure 18**. The optical micrograph shows that the structure is mainly austenitic with some martensite along the eutectic carbides and in the eutectic matrix.

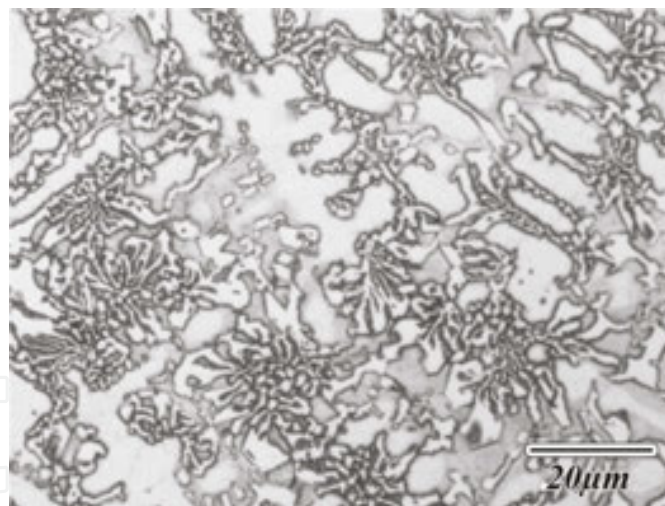


Figure 18. As-cast structure of a high-chromium white cast iron.

Although the chromium content of many Hi-Cr white iron alloys is quite high (typically between 12 and 30%), the majority of this is combined with carbon in the carbides. The chromium content remaining in the matrix is therefore quite low. For instance, Laird et al. [60] measured a matrix chromium content of only 9.5% in 17.8%Cr-3%C iron using electron microprobe analysis and De Mello et al. [61] obtained 9.5%Cr in the matrix of a 16.1%Cr-3.26%C. In the same way, Dogan et al. [62] obtained a value of 16.2%Cr in the matrix of a 26%Cr-2.76%C. Then, additional alloying elements are required to achieve sufficient

hardenability, particularly with larger section sizes [63]. The most common elements used for these additions are molybdenum, nickel, manganese and copper.

Molybdenum is added to high-chromium white irons in amounts between 0.5 and 3.5%. Although it is believed that amounts greater than 1% are required to be effective [64], additions of more than 3-4% achieve little [65]. It acts to suppress pearlite formation and increase hardenability [61, 65, 66] by effectively inhibiting secondary carbide precipitation during cooling. Molybdenum also has a synergistic effect on the influence of other alloying elements such as nickel and copper, which are more effective in delaying pearlite formation if added in conjunction with molybdenum [61, 66–69]. Part of the molybdenum in the irons forms a eutectic carbide of the type M_2C at the final stage of solidification [61, 65, 66, 70–72]. Another advantage of molybdenum is that it has little effect on the M_s temperature [73], while most elements tend to decrease the M_s temperature possibly leading to over stabilisation of austenite.

Nickel, manganese and copper are added to these irons mainly to improve hardenability. They are commonly found in amounts up to 2%. Nickel and copper partitioned to the matrix [51], while manganese may be partly dissolved in matrix and partially segregated to the carbide phase, which reduces its effectiveness. These elements contribute to lower the M_s temperature of austenite during cooling and therefore increasing the alloy content often produces more austenite which in turn represents a decrease in the as-cast hardness [67]. When nickel is added to the iron along with molybdenum, the effectiveness in improving hardenability is quite considerable and the undesirable pearlite formation is avoided [67].

Less traditional alloying elements such as vanadium, tungsten, titanium and niobium have also been added to white iron alloys [45, 46, 64, 70, 74–80]. The aim of these additions is usually to achieve some modification of the eutectic carbide structure by obtaining harder carbides, though they may improve the hardenability of the matrix.

The eutectic carbide structure in Hi-Cr irons is strongly influenced by chromium as this is a strong carbide-forming element. It has been pointed out by Pearce [81] that as the chromium content increases above 10-12%, the type of eutectic carbide that forms changes from M_3C to M_7C_3 . For both types of eutectic carbide, increasing the chromium content of the alloy increases the proportion of chromium to iron as the metal species in the carbides [82], while also, increasing the carbide hardness.

It has been recognised that a possible strategy for improving the toughness of white iron alloys as well as the wear resistance under sliding conditions involves the refinement of the eutectic carbide structure by producing finer, more globular carbides [81, 83, 84].

Alloying additions have also been used to modify the eutectic carbide structure [60, 85–94]. Generally, attempts to modify the eutectic carbide structure through alloying elements have had limited success. Boron has been used within the range of 0.1-0.3% [91, 92] with this purpose. The argument is the thought that the presence of boron in iron alloys decreases the solubility of carbon in austenite; which may conduct to a higher and fines carbide precipitation during solidification. The effect of silicon and rare earth elements has been investigated in these irons, in the case of silicon due to its effect on transformation behaviour, and in the case of rare

earths due to its high segregation effect. Results of these elements on the carbide structure have produced inconsistent results.

The formation of other type of carbide, such as niobium carbide [78] and vanadium carbide [90], though the appropriate alloying additions, has been associated with the formation of finer rounder carbides.

The commonly applied heat treatment to destabilise the austenitic matrix, according to Pearce [81], involves holding at a temperature between 920 and 1060°C for 1–6 h. During soaking at these temperatures, secondary carbides precipitate in matrix reducing its alloy content, particularly the amount of carbon. If the alloy content is too low in austenite, the M_s temperature increases [69] and a higher amount of austenite will transform to martensite during subsequent cooling down to room temperature. For these alloys, air cooling after destabilisation heat treatments is usually a common practice to produce a predominantly martensitic structure and the risk of cracking by rapid cooling is avoided [81]. **Figure 19** shows a micrograph of the structure of a destabilised Hi-Cr iron 17%Cr-2.5%C-2%Ni-2%Mo, which was held at 1000°C for 45 min and air cooled to room temperature. The structure is composed of the eutectic carbides, and the former austenite has transformed to martensite and secondary carbides.

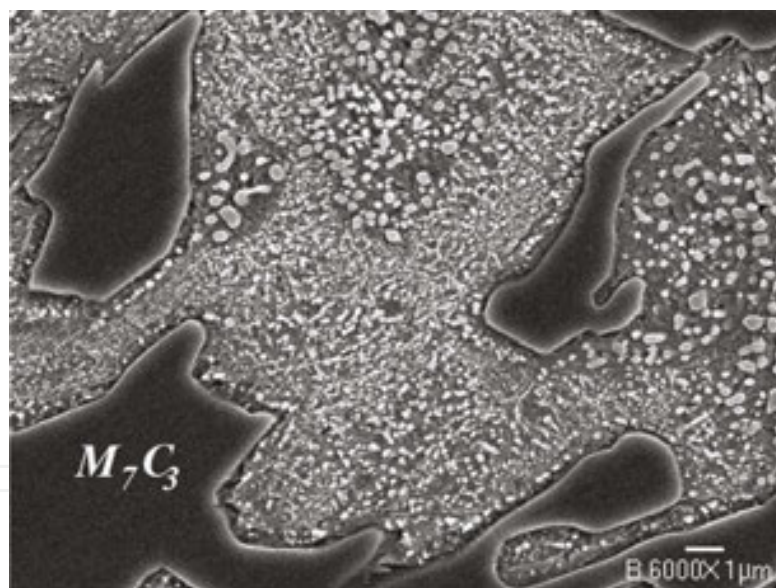


Figure 19. Microstructure of the heat-treated high-Cr white iron.

Although a predominantly martensitic matrix is formed after destabilisation treatment, retained austenite may be present in amounts up to 35% [95–97]. According to Tabret et al. [52], the retained austenite volume depends on the amount of dissolved carbon after the destabilisation heat treatment. Dissolved carbon content in austenite is in turn influenced by the composition of the alloy, the time and temperature of heat treatment and as well as the thickness of the cast. Eutectic carbides, on the other hand, are unaffected at the temperatures of the destabilisation heat treatment.

It has been widely accepted the relationship between bulk hardness and wear resistance for most alloys under abrasive conditions; according to the *Archard's Law*, the harder the material, the more the wear resistant it is. However, as Tabret et al. [52] have pointed out, there are many factors influencing the abrasive wear resistance of an alloy for a given wear system. These include the following: load, type of abrasive material, speed, etc, and then, they suggest that the microstructure of the alloy must play a strong role on the overall abrasive wear behaviour.

The eutectic carbides in white iron are main responsible for the excellent wear resistant of these irons when compared with other alloys. The eutectic carbide volume fraction is commonly between the range of 20 and 35% in the microstructure of hypoeutectic high-chromium white irons. It could be thought that increasing the carbide volume fraction would increase wear resistance; however, some other factors such as carbide type and hardness, orientation, and the role of the matrix as a carbide supporter may determine the overall wear behaviour [52].

The effect of carbide type and hardness could be considered negligible since not much difference in hardness has been observed in Hi-Cr white irons and the abrasive materials generally used in laboratory tests. High-chromium white irons commonly form the M_7C_3 carbide as the eutectic carbide. The addition of niobium and vanadium to Hi-Cr white irons to form even harder carbide types has been shown to improve the abrasion resistance [77–79] due to the increase in the relative hardness, as shown below.

On the other hand, the carbide volume fraction (CVF) clearly influences the abrasive wear resistance of these irons. Although we could expect an increase in wear resistance when increasing the amount of the carbide phase, the wear system along with the wear mechanisms taking place determines the actual wear behaviour of the alloy under abrasive conditions [52].

From the asseveration of the main role of the carbide phase on the abrasive wear resistance, it could be thought that the roll of the matrix is just to protect or provide mechanical support to the carbides. However, the actual roll of the matrix in these irons must be much more complex, according to Fulcher et al. [98]. They suggested that the roll of the matrix depends on the protection level that carbides provide to the matrix during abrasive wear. If the abrasive particles are larger than the mean free path of carbides (matrix region between carbides), the main roll of the matrix is to provide mechanical strength to the carbides. However, if the abrasive particles are small enough to abrade the matrix, it is preferentially removed and the naked carbides become unsupported and prone to crack. When this happens, the abrasion resistance of the matrix is of main importance, as this controls the rate at which the carbides become unsupported and fracture [52].

Most studies on the effect of the matrix structure have compared the as-cast, predominantly austenitic matrix with the heat treated predominantly martensitic matrix [99–101]. And it has been established that a pearlitic matrix reduced the abrasion resistance, due to poor support of the carbides, and this matrix structure is generally avoided if good abrasion resistance is required.

Under this basis, the precipitation of secondary carbides within the matrix of high-chromium white irons may also influence the abrasion behaviour. These secondary carbides strengthen

the matrix by a dispersion hardening effect therefore increasing the mechanical support to the eutectic carbides and, in turn, leading to improved wear resistance [79].

Carbide-forming elements such as titanium, niobium, vanadium and tungsten have been widely used as alloying elements in high-chromium white irons. These elements either partition to the eutectic carbide phase or form their own carbides. In any case, the overall hardness of the iron is increased. In the particular case of niobium, it forms hard niobium carbides that improve hardness and abrasive resistance.

The influence of niobium (from 0 to 2.06%) on the microstructural characteristics of a 16.7%Cr white iron was examined in both as-cast and heat-treated conditions [78]. The as-cast structure of the Fe-Cr-C alloy consisted of primary dendrites of austenite and the eutectic austenite- M_7C_3 . Fe-Cr-C-Nb alloys also contained various amounts of NbC. In alloys containing up to 1%Nb, NbC carbides were present in the petal-like form, whereas in the alloy with 2.06%Nb, they were in the compact shaped form.

Reaustenitising the as-cast structure resulted in the precipitation of secondary carbides and depletion of carbon in the matrix, which transformed a large amount of austenite to martensite during quenching to room temperature. The amount of retained austenite was minor in the alloys containing niobium. Niobium increases the amount of NbC while decreases the amount of M_7C_3 . These carbides also became elongated as the percentage of niobium increased which increases hardness and wear resistance.

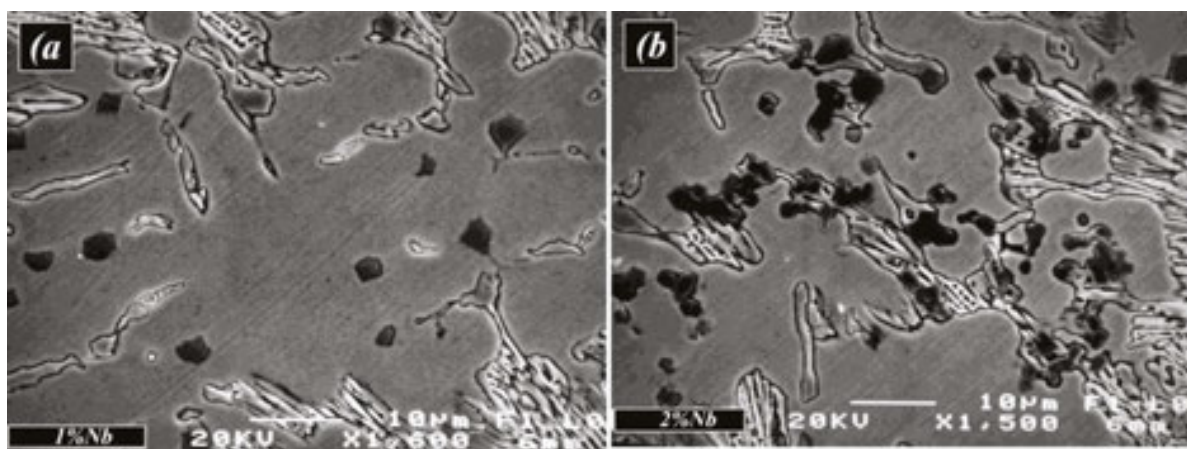


Figure 20. Niobium carbides in high-chromium white iron. (a) 1%Nb, most of the carbides are within the matrix, (b) 2%Nb, the carbides are agglomerated and segregated to the eutectic carbide/matrix interface.

Niobium in Fe-Cr-C-Nb alloys forms carbides of the type MC. According to some authors [45, 46, 102], the solubility of niobium in austenite or M_7C_3 is very low, so the majority of niobium present in the alloy is in the form of MC carbides. These carbides are formed before M_7C_3 , which causes depletion of carbon in the liquid. Since carbon is the primary element that determines the amount of carbide in high-chromium irons, the amount of M_7C_3 carbide should decrease as the Nb increases. Furthermore, the decrease in the M_7C_3 carbide due to the increase in niobium reduces the amount of chromium to form such eutectic carbide and more chromium

remains in austenite increasing its hardenability. They also suggest that the presence of NbC contributes to a reduction in the size of the M_7C_3 due to a change of the solidification sequence, and this increases the fracture toughness of the alloy.

The microstructure when adding niobium always shows the presence of the NbC particles embedded in the matrix or segregated to the interface matrix/eutectic carbide, depending on the amount of niobium in the alloy (see **Figure 20**).



Figure 21. SEM micrographs showing the worn surface of an as-cast white iron after an abrasive wear test at three different loads, and evidencing the increase in roughness as load increases. The arrows indicate the wear direction [103].

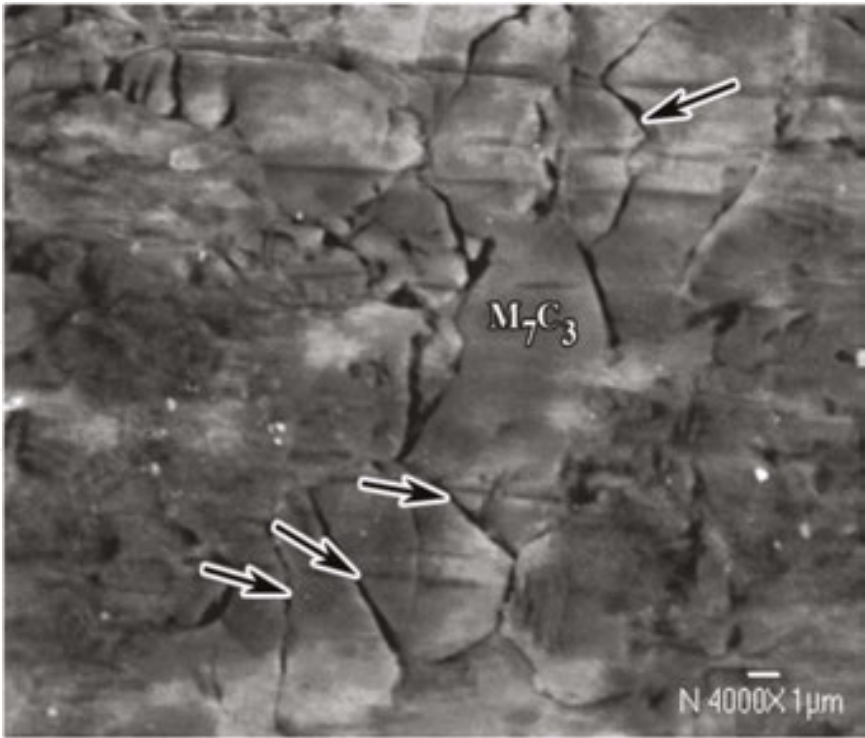


Figure 22. SEM micrograph showing carbide cracking at the surface of an as-cast iron after wear test under 54 N load [103].

The presence of such carbide particles in the structure has proven to increase wear resistance either under sliding and abrasive conditions. The effectiveness of the primary carbides and the strengthening of matrix by the heat treatment are the cause of the better wear behaviour these alloys. For example, **Figure 21** shows a series of SEM micrographs of the worn surface of a 3.1%C-17%Cr-1.1%Ni-0.98%Mo iron alloyed with 2%Nb-1.8%Ti-2%V in the as-cast conditions for different applied loads during an abrasive wear test [103]. From this figure, as the load increased, the wear grooves were more evident. Also, for high loads carbide cracking commonly occurred, particularly for the as-cast iron. The soft matrix, highly deformed by friction during wear provides low support to the carbides and they crack (**Figure 22**); on the other hand, for heat-treated irons carbide cracking is less common since the strengthened matrix allows minimum deformation. These observations indicate a more stable matrix supporting the carbide phase in the alloyed iron due to the presence of MC carbides.

Figures 23 and **24** show SEM micrographs of the cross section of the iron without the alloying Nb-Ti-V elements in both as-cast and heat-treated conditions (**Figure 23**) and of the alloyed iron also in both as-cast and heat-treated conditions (**Figure 24**) after being wear tested with loads of 25 and 54 N. (analysed in Ref. [103]). From these micrographs, higher levels of deformation and carbide cracking are evident for the as-cast iron and particularly for the higher applied load; this destabilises the surface and contributes to higher wear rates. On the other hand, low deformation of matrix and no carbide cracking are observed for the heat-treated alloys, particularly for the alloyed iron (see **Figure 23d**), contributing to higher wear resistance. Although the depth of deformation was not measured for these alloys, due to the friction forces, the depth at which carbide cracking can be observed should increase with load. In the alloyed irons, one feature that highly contributes to lower eutectic carbide cracking is the presence of the hard MC carbides that strengthen matrix, even in the as-cast conditions. This phenomenon of subsurface destabilisation by carbide cracking during wear tests has been widely analysed and reported first by Fulcher et al. [98] and then by some other authors [79, 104, 105]. This is a very important factor to consider when analysing wear resistance of white irons and some alloys with a massive brittle ceramic phase in the structure.

Under these basis, for the analysed irons by Bedolla-Jauinde et al. [103], a considerable increase in wear resistance should be expected for the alloyed heat-treated iron. However, according to them, the increase was moderate and this has been attributed to the abrasive conditions used for the test. Based on the roll of the matrix during abrasive wear tests described by Fulcher et al. [98], and on the asseverations of Zum Gahr and Doane [99] that martensitic matrices obtained by heat treatments in these irons improves the wear behaviour under low stress abrasion, Bedolla-Jacuinde et al. [103] describe the behaviour of the analysed irons. The martensitic matrix reinforced with secondary carbides and with primary MC carbides reduces wear of matrix and minimises carbide cracking. This metallurgical phenomenon has been widely reported to improve the wear behaviour of high-chromium irons either under sliding and abrasion [52, 79, 98, 104, 106].

The wear behaviour of the irons analysed by Bedolla-Jacuinde et al. [103], particularly at higher loads, seems to be determined mainly by the eutectic carbide volume fraction and matrix has a minor effect. An additional important factor to consider is the eutectic carbide alignment

with the surface. Dogan and Hawk [106] have reported superior wear resistance under high stress abrasion for irons that have carbides aligned parallel to the surface, compared with the same irons with carbides aligned perpendicular to the surface. They argue that long carbides perpendicular to the surface are more prone to bend and crack, particularly close to the worn surface, where the plastic deformation of matrix is considerable. Carbide cracking was observed by Bedolla-Jacuinde et al. [103] and is shown in the micrographs shown from **Figures 23** and **24**. They explain that the bending of carbides aligned perpendicular to the surface is caused by the friction generated by the surfaces in contact, and during bending, as highlighted by Fulcher et al. [98], tensile stresses are developed at the back side of the carbides. Such tensile stresses along with the matrix deformation may conduct to the carbide fracture and the consequent surface destabilisation.

A general conclusion established by Bedolla-Jacuinde et al. [103] for explaining the better wear behaviour of the iron alloyed with niobium and titanium was the higher carbide volume fraction compared with the unalloyed iron. These include hard primary MC carbides within the matrix and the eutectic M_7C_3 carbides. Furthermore, the improved wear resistance observed after heat treatment was also attribute to the strengthening of the matrix, which transformed from austenite to a complex mixture martensite plus some retained austenite a high amount of tiny secondary carbides.

As a summary, niobium in cast irons has been particularly used in low amounts as a carbide-forming element to increase hardness and basically wear resistance of these alloys.

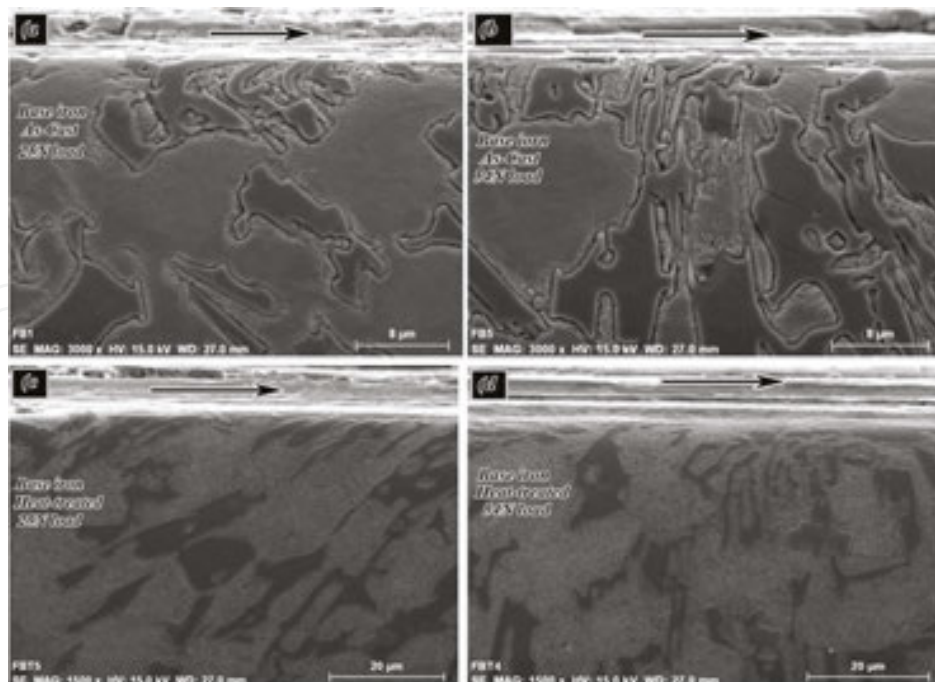


Figure 23. SEM micrographs showing the structure below the worn surface in both as-cast (a and b) and heat-treated conditions (c and d) of the unalloyed irons analysed in Ref. [103].

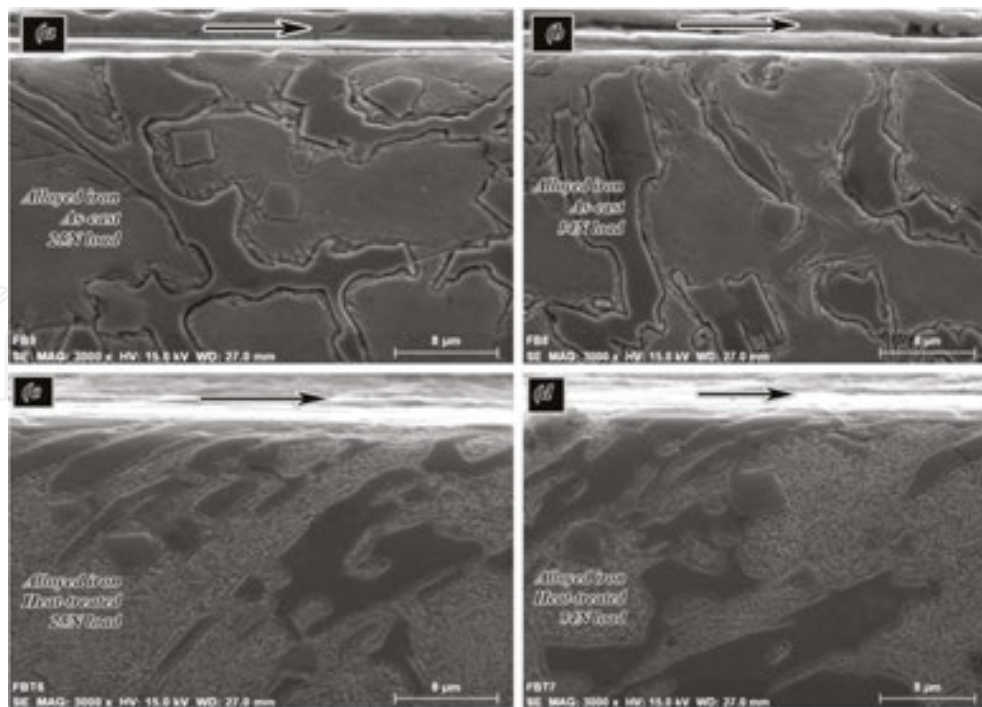


Figure 24. SEM micrographs showing the structure below the worn surface in both as-cast (a and b) and heat-treated conditions (c and d) of the alloyed irons analysed in Ref. [103].

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