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Cast Irons, an Historically Green Material Worthy of Continuous Research

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Abstract. Throughout history, cast iron is unique amongst metallic materials. No other metal can boast such a long history, together with such a wide diversity of variants, properties and applications. Arguably, no other material can claim to have such complexity. While the cast iron foundry routinely churns out myriad components, through weekends and on night shifts, a supporting cast of researchers and engineers have humbly ensured a choreography of carbon atoms that could make the busiest beehive look lethargic. We control the carbon atoms not with furnaces and wirefeeders, but with knowledge. This knowledge enables a material with a unique combination of design flexibility, mechanical properties, wear resistance, recyclability, low life cycle energy consumption, and low cost. And it will be with the continued pursuit of understanding and knowledge that tomorrow's researchers and engineers will ensure the continued growth of new material variants, with improved material properties and new applications that make the world a better place. Cast iron: thousands of years of development and progress behind us; thousands of fascinating mysteries and opportunities ahead of us.

Keywords: Cast irons; History; Market share;

1. Introduction

Cast irons are easy to shape materials whose properties have evolved over the years following technical and scientific improvements. As of 2018, cast irons represent 70% of the 110 Million tons of metals being cast each year in the world (10% for cast steels, 20% for aluminium and other alloys) [1]. Cast irons are recyclable materials at low cost and with relatively limited pollution when compared to their present-day competitors. This is schematically illustrated in Fig. 1, where so-called grey cast irons are compared with cast steels and aluminium alloys in terms of price per MPa of Yield strength, vs. embodied energy (Fig. 1-a) and CO_2 footprint (Fig. 1-b). The latter two terms mean energy used and CO_2 emitted, respectively, for primary production, casting and recycling of 1 kg of alloy.

Even far before dollars were established as a universal reference, and far before aluminium could be thought of, cast irons were already quite attractive for several applications in agriculture, domestic applications and decoration. Cast irons are in fact historical materials that have appeared at the Iron Age when the temperature in the furnace for processing iron ore became high enough. It is thus of first interest to have a rapid look at the evolution of cast iron materials over the time until the modern era, this is rapidly done in the historical section to follow. As with all other materials, several important steps have been taken over the last two centuries in the processing of cast iron, in casting technology and in the cast iron itself; these are mentioned in the following sections.

Nowadays, cast irons are a family of materials as depicted in Fig. 2. Two main branches can be defined depending on the carbon-rich phase, which can be either cementite and other carbides or graphite. Alloys within this former branch, also called white cast irons for the colour of the rupture surface, have good wear properties and good heat and corrosion resistance when alloyed, but they are brittle. This branch is however a

minor part of the family and most of the current production consists of grey (or graphitic) cast irons in which the carbon-rich phase is graphite giving a dark contrast to rupture surfaces. The vast majority of these irons are based on Fe-C-Si alloys and thus could be called silicon cast irons. These irons are the focus of this work. Ni-resist graphitic cast irons are heat and corrosion resistant, while very high-Si alloys are corrosion resistant. Behind the sorting in Fig. 2 is a continuous evolution of cast iron alloys and their processing, as described in the section "Main Steps".

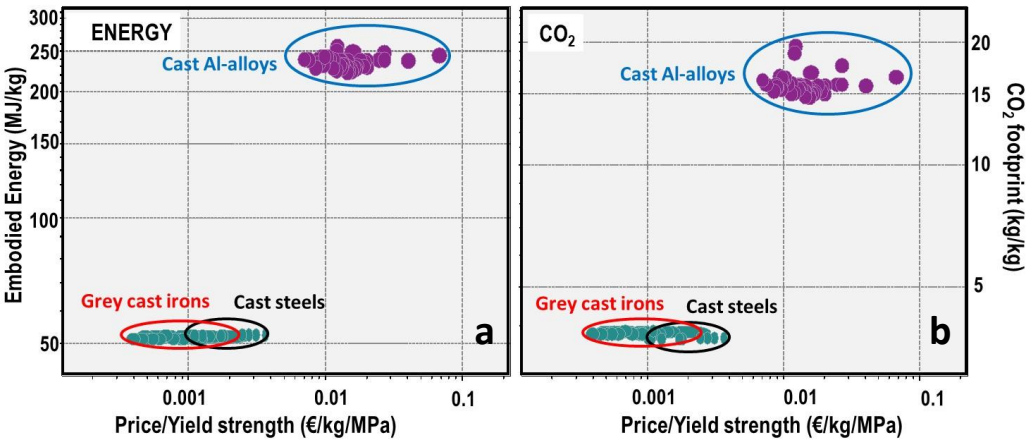


Figure 1 Grey cast irons compared with cast steels and aluminium alloys in terms of price and environment impacts; x-axes concern the ratio between price and Yield strength, while y-axes concern estimations of energy used (a) and equivalent CO_2 emissions (b) for the primary production, casting and recycling of one kg of alloy. Data from [2].

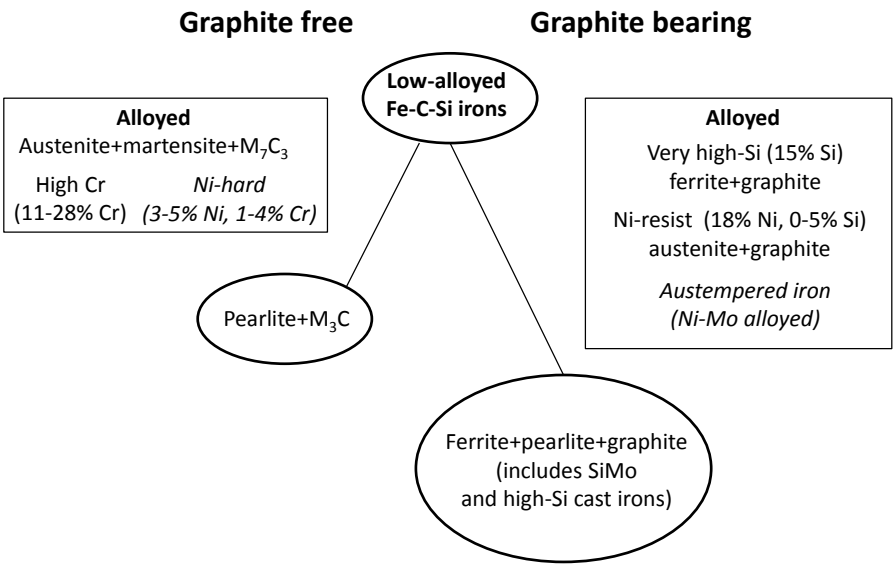


Figure 2 The cast iron family with the basic microstructures indicated. They are all obtained in the as-cast state, except those appearing in italics that are subjected to specific heat-treatment (after Elliott [3] and Stefanescu [4]).

The properties of silicon cast irons are determined by their microstructure after the two following phase transformations: 1) solidification during which the graphite shape is determined; and 2) solid-state transformation of the Fe-rich matrix in ferrite or pearlite. With low levels of Ni and Mo, silicon cast iron can be austenitized (austempered) and then transformed at 300-450°C to give a matrix of ausferrite. This material is called austempered ductile iron (ADI) and has very high mechanical properties. The present

market share and the associated concerns are presented in a section dedicated to production and concerns. These concerns are associated to on-going laboratory researches and are challenging, in particular because of the increasing demands for weight reduction and increased loading together with an ever-increasing number of recycling loops compounding the effect of trace elements on the parameters controlling the microstructure. Some of the up-to-date challenges are discussed in a last section.

2. A very brief history

Legend reports that, "approximately 4,000 years BC, scientists and sages commissioned the first iron cupolas. These early metallurgists placed a curious metal-like substance, which we now know as iron ore, in the hollow of a burnt out tree trunk. The charred inner surface of the trunk provided fuel for the fires and thermal insulation, while random holes that burned through the trunk allowed the ambient winds to enter and feed the charcoal. With the right combination of wind, rich ores and extra charcoal, the charge was reduced to a metallic iron sponge that could be rolled, using rocks, into decorative beads. It was 6000 years ago, and iron was more highly valued than gold." [5].

This is more or less what historical works describe which locate the very start of iron history in Anatolia (Armenia) or Mesopotamia (Iran) [4, 6], or else China [7]. It is worth noting that independent development in sub-Sahara Africa at the same time was postulated and is now well documented [8, 9]. A short but comprehensive presentation of the beginning of iron ore processing, and of the parallel development of iron and cast irons, has been published by Le Coze [6]. Production techniques and raw materials were gradually refined as the Iron Age evolved. Iron implements and weapons began to appear in approximately 3000 BC, and the comparatively advanced technique of hardening iron weapons by heat treatment was known to the Greeks by about 1000 BC.

As the temperature of the furnaces was progressively increased and reached 970°C (Fe-C-P eutectic), 1154°C (Fe-C eutectic) and above, some liquid may have formed which was certainly mixed with scoriae. Increasing further the temperature slightly above 1200°C allowed reaching the FeO-fayalite or fayalite-SiO_2 eutectic, meaning the dross and scoriae became partly liquid and could be separated more easily from the iron loupe. In most production locations, this carbon enriched liquid iron – the ancestor of cast irons - was eliminated except in China where the first crafts, tools and weapons made of cast irons date back to 600-500 BC [4, 7]. This means that it was early understood that the furnaces could be conducted either to give "wrought" iron for further refining by hammering to give steel, or to give carbon-rich iron liquid that was suitable for casting. In this latter case, adding minerals (clay, shells, ...) changed the scoriae into a slag protecting the metallic liquid and thus keeping its casting ability while more of the charge was melting. It is probable that some silicon dissolved in the liquid, in an amount that increased with the temperature, and that it was early understood that solidification with fast cooling rates resulted in brittle components while slower cooling yielded enough ductility to keep the cast parts in one piece when handling them. This historic development of cast irons in China contrasts with the fact that cast irons became recognized in Europe only during the 14th century AD.

Cast iron was such an "easy" material to process that it soon allowed gigantism. This applies to the use of cast iron that was selected to erect impressive sculptures such as the Cangzhou lion in Fig. 3 or the famous pagoda in the Yuquan temple. With some delay, the same happened in Europe with the 35 km of cast iron pipes and other components that were installed during the second part of the 17th century to bring water to the dozens

of jets in the garden of the Versailles castle [10] so as to satisfy the egocentrism and megalomania of one single human being.

Figure 3 Iron lion of Cangzhou, 953 AD.
http://images.china.cn/attachement/jpg/site1007/20111020/000cf1a48f871009d8af52.jpg

The development of cast iron followed the progress of iron processing which is nowadays known in detail with the evolution in Europe of the Catalan forges to larger and larger blast furnaces. The state of the art at the beginning of the 19th century has been described by Karsten [11], including a detailed description of the work by de Réaumur at the beginning of the 18th century on the solid-state heat treatment of cast irons to give malleable cast irons and cemented iron. The two routes for making steel, i.e. the direct reduction through a pasty state that gave "wrought" iron and remelting and oxidizing of cast iron, were both used until the development of the Bessemer's converter. Although the metallurgy was not understood, and Bessemer wrongly concluded that air was fuel as many before him [8], the breakthrough was realised and steelmaking could leap from kilograms per day to tonnes per hour. This is only with the publication of the first Fe-C phase diagram at the very end of the 19th century that it was clearly understood that "wrought" iron, steel and cast irons belong to the same family.

Iron ore processing used huge amounts of charcoal so that optimizing it became a necessity certainly very early, and this implied increasing the maximum furnace temperature. To achieve this, blast furnaces have become increasingly taller with better and better control of the air blown onto the charge. In the early 18th, charcoal started to be replaced by coke for its better mechanical properties with the drawback of adding sulphur to the melt. For later processing, the liquid cast iron could be tapped into a trough made in the sand floor of the foundry and flowed into impressions made by the foundryman's foot on either side of the trough. Because the orientation of the foot-sized ingots along the trough resembled piglets feeding at a sow, the small ingots became known as pig iron.

Even though cast iron metallurgy was not yet mastered, casting technology was already in an advanced stage. This is illustrated with Berlin iron (fer de Berlin) jewellery that came in fashion during the early 1800's when Prussia needed to finance their war against Napoleon. The Prussians were asked to turn in their gold jewellery to raise funds for the war and were given iron jewellery in return. Berlin iron was sand-cast and then lacquered black. Many such pieces can be found in museums in Continental Europe, but

also in Brazil where the fashion was exported at the same time the country built its first blast furnaces; see Fig. 4.

Figure 4 Brazilian cast iron necklace following the fashion known as Berlin iron, early 19th century [12]. With permission from Irina Aragão and Anais do Museu paulista (Brazil).

At the same time, cupolas and other kinds of furnaces for melting and processing irons and steels developed. In present days, blast furnaces define facilities providing pig iron for immediate use, particularly in integrated steel mills. Cupolas, in contrast, were designed for manufacturing stocks of cast iron to be processed later. They evolved along the time and became the most usual means to melt the charge in foundries. Today, high volume foundries use a combination of cupola and electric induction furnaces to melt the iron. The melting costs of both techniques are similar, but the cupola has a productivity advantage. Large cupola furnaces can melt more than 100 tonnes per hour from a single furnace while the largest induction furnaces can only produce approximately 20 tonnes per hour. Despite the productivity advantages, the cupola will eventually be relegated to the history books. In Europe, the cupola will likely be phased out by 2050 as part of the Net Zero European Green Deal. Good for the environment, but potentially devastating for the European foundries who must continue to face international competition.

3. The main steps during the modern era (Anthropocene)

Being optimistic, scientific and technical understandings are intermixed with industrial progresses, though these latter may often be leading for economic concerns. As for iron and steel, this was put in an historical perspective by Le Coze who stressed the technical evolution between 400 BC and 1400 AD in contrast to the explosive and parallel scientific and technical changes since then [6]. The advent of chemical analysis, microscopic observations and other metallographic tools such as X-rays supported the improvements of materials properties.

Until the 19th century, the composition of the cast parts was given by that of the iron ore [13] and also, though not understood at that time, by the minerals added to generate the slag. The importance of the slag composition for limiting iron loss (as FeO) and to remove sulphur from the coke and phosphorus from the ore has developed progressively, mostly in the 20th century. Slag is most generally described by its basicity which is the ratio of basic oxides (CaO, MnO, FeO, Na_2O) over acid oxides (SiO_2, P_2O_5). By controlling the composition of the slag and the temperature at the metal/slag interface, it is possible nowadays to get out of the blast furnace a cast iron with the desired silicon content. Beyond the cast iron industry, modern steelmakers have taken slag science to new

heights, leading to the expression: “take care of the slag and the iron will take care of itself”.

Until the mid of the 20th century, the main concern was low ductility and associated moderate tensile strength because of the lamellar shape of graphite, see the bottom-left micrograph in Fig. 5. In the 1940s, following earlier attempts in Germany, Morrough and Williams in England and Millis and co-workers in America sought a way to ball graphite. The British (at BCIRA) found that additions of less than 0.1% cerium were sufficient to cause the graphite to grow in the form of individual spheroids instead of flakes. The Americans (at Inco) found that additions of approximately 0.05% magnesium would do the same thing. The Inco magnesium process eventually won the battle on technical grounds and the annual worldwide production of spheroidal graphite (aka nodular graphite or ductile) iron (SGI) has since grown to more than 25 million tonnes.

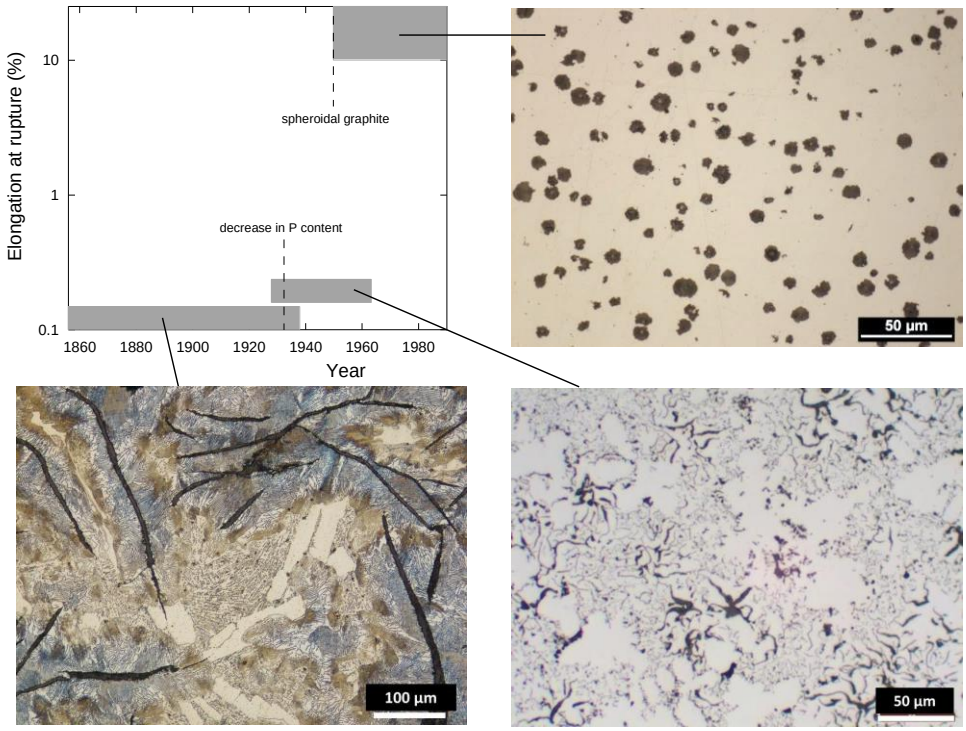


Figure 5 Evolution of the elongation at rupture of cast iron used for water pipes (adapted from Lesoult et al. [14]) and of their microstructure. Graphite appears in dark contrast in the micrographs. The samples were etched so as to reveal the constitution of the matrix, which is pearlite in the historical material (with some coarse eutectic cementite) and ferrite in the two centrifugally cast pipes. Note that centrifugally cast LGI and SGI are both heat treated for full graphitization just after casting.

The modification of the graphite shape from flakes to nodules had a profound affect on the properties and the market potential of cast iron. In comparison to grey iron, the tensile strength tripled, the stiffness increased by 50% and ductility or elongation changed from nearly 0% to more than 5%, and up to more than 25% with a ferritic matrix. This quantum step in cast iron technology is illustrated in Fig. 5 for the case of cast iron pipes manufactured by the Pont-à-Mousson company that was created in the mid of the 19th century. This figure presents the parallel evolution of the elongation at rupture and of the microstructure of the cast irons. The microstructure at the turn of the 20th century was certainly much alike that of Versailles' pipes that is illustrated here. Brittleness of cast iron

parts was a concern, not only because of the lamellar shape of graphite, but also because the parts contained large precipitates of eutectic cementite and some phosphides. The treatment of the melt or the selection of iron ores allowed halving the phosphorus content and thus suppressed phosphides. At about the same time was introduced the centrifugal process in which the melt is poured in a water-cooled and rotating metallic die. This led to a significant refining of the microstructure of lamellar graphite irons (LGI), in particular by shortening the graphite lamellae. The dramatic change in the 1950 is due to the switch to SGI instead of LGI.

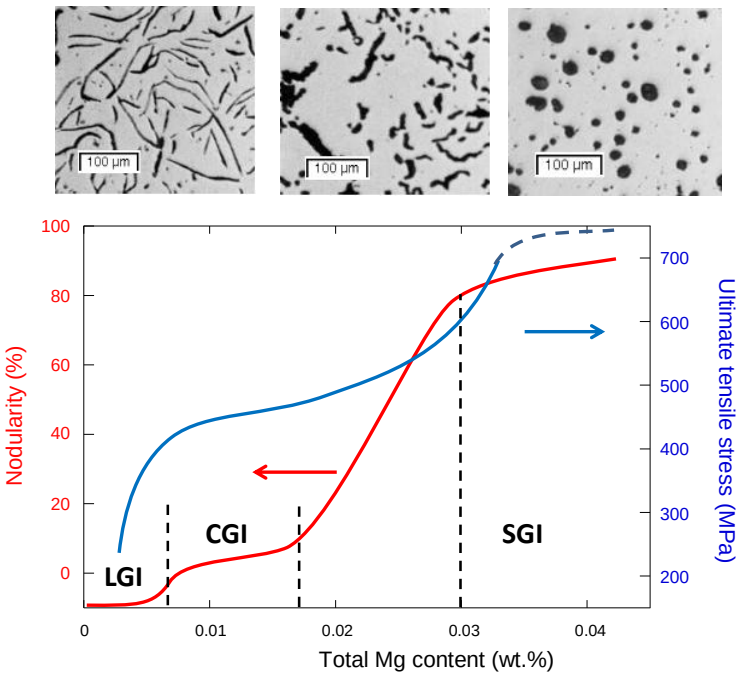


Figure 6 Evolution of graphite shape and UTS (pearlitic matrix) with Mg content, illustrated for a base iron sulphur content of 0.013% [17].

Millis et al. also received a patent in 1949 for a grey iron having improved properties because graphite assumed a more compact shape than usual flakes. The compact graphite shape was achieved by adding a controlled amount of magnesium, and such irons became later known as compacted graphite irons (CGI). Interestingly, the patent was applied for in 1948 on the same day as Millis' more famous ductile iron patent, and the two patents were granted on the same day in 1949, with US patent number US2485760 for SGI and US2485761 for CGI. CGI has better mechanical properties than LGI and is much less prone to microporosity than SGI. Critically, for modern engine applications, CGI also has higher thermal conductivity than ductile iron. However, it was only in the 1960s that it was found interesting to purposely generate this intermediate graphite form, see the review by Nechtelberger et al. [15]. CGI has thus been in use for a long time but this was only for niche applications until the development of a proper thermal analysis control of melt preparation just before casting. The first series production of CGI engine for passenger vehicles was launched by Audi in 1999 and since the beginning of the 21st century CGI is breaking the market of automotive engines and components, though not yet appearing as such in production trends that differentiate data only considering LGI, SGI and malleable irons [16].

Nowadays, graphite is industrially spheroidized by simultaneous addition of magnesium and rare earths (RE). In contrast, there are several ways to generate compacted graphite as reviewed by Nechtelberger et al. [15]. However, the most usual is by limited additions of Mg and RE when compared to SGI. Figure 6 shows the change in graphite nodularity as function of Mg content [17], with indication of the domains and typical examples of graphite shape for LGI, CGI and SGI. Note that the nodularity was set negative for lamellar graphite to emphasize that the industrial nodularity scale is defined for compacted and spheroidal graphite and not for lamellar graphite for which letters (A-E) are used to differentiate the various shapes [18]. The evolution of ultimate tensile stress (UTS) with nodularity for 85-100% pearlitic cast irons is also illustrated.

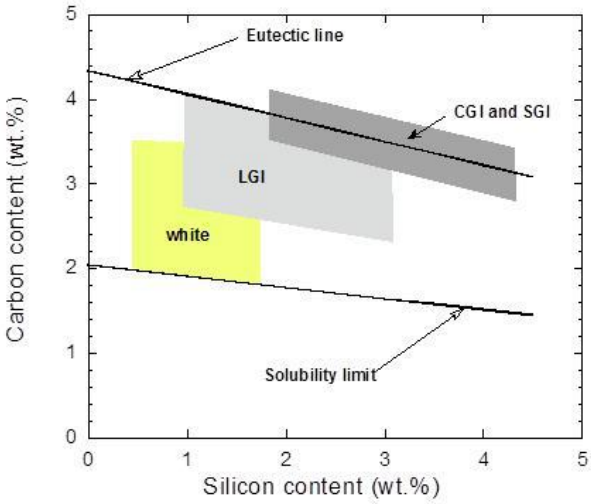


Figure 7 Carbon and silicon composition ranges of silicon cast irons (adapted from Elliott [3]).

The composition of most of the silicon cast irons is selected on the basis of the graphite shape as illustrated with Fig. 7 adapted from Elliott [3]. This graph shows the projection of the iron-rich corner of the Fe-C-Si diagram with the solubility limit of carbon in austenite (at eutectic temperature) that defines the lower limit of the cast irons domain. The upper limit is at carbon contents slightly larger than the eutectic line. White cast irons are low-silicon hypo-eutectic alloys and are more and more replaced by high-Cr cast irons for wear properties. Their use is mostly limited to manufacture malleable irons by heat-treatment. LGI is mostly hypoeutectic, with the austenite dendrite network guaranteeing a minimum rupture elongation. If LGI could be made with higher carbon content, the industry would do it to maximise thermal conductivity. But there is a need to restrict the carbon content to ensure (i) that the graphite doesn't cause brittleness, and (ii) that there is enough austenite to carry the load and compensate for the ill-effects of the graphite. CGI and SGI are near-eutectic alloys for minimizing microporosity.

The trend for higher silicon content for SGI and CGI started in the early 1980s with the development of the so-called SiMo cast iron for exhaust manifolds. Higher Si content raises the eutectoid temperature and thus increases the maximum service temperature while Mo is added as it gives rise to a network of eutectic carbides that improve creep properties. However, as exhaust temperatures continue to rise to satisfy emissions requirements, SiMo exhaust manifolds and turbocharger housings are being widely replaced by stainless steels that do not incur a phase transformation. These higher temperature capabilities outweigh the fact that oxide scales are generally better adhering on cast irons than on steels.

Since the 2000s, high-silicon SGI has developed as the yield stress and ultimate tensile stress are linearly increasing with Si concentration because of partial ordering of the ferritic matrix. Mechanical properties similar to pearlitic irons may thus be obtained with the advantage of decreasing tool wear during machining because the matrix is more homogeneous. More generally, there is a wealth of research for improving mechanical properties of the matrix of cast irons. Amongst the many possibilities that have been considered, austempered cast irons are slowly showing great industrial potentialities.

4. An overview of present cast iron production and concerns

Cast irons are found in pipes, machinery, railway, automotive and energy industries, as well as in cooking and ornaments in public areas, etc. Figure 8 differentiates the market share for SGI (about 25 million tonnes per year) and LGI (about 50 million tonnes per year) based on the 2018 USA data [19] that are certainly representative of the world market.

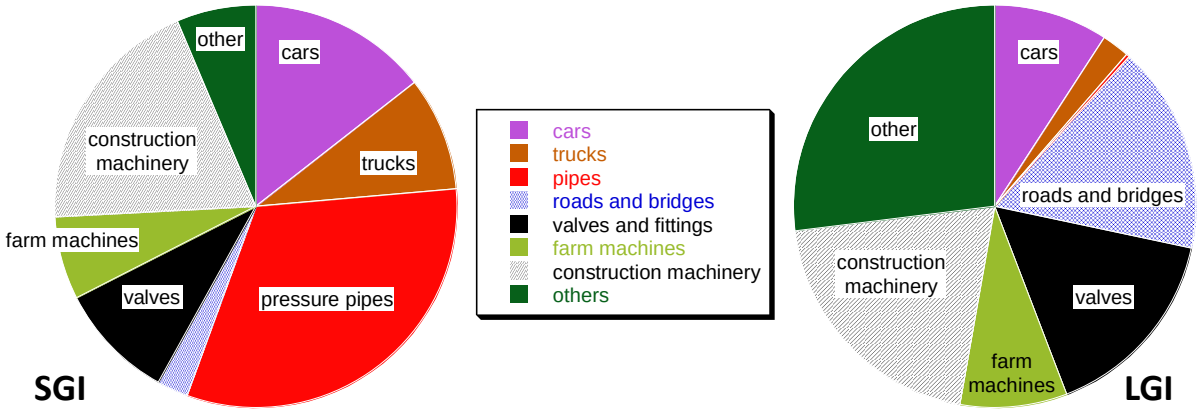


Figure 8 Market distribution in USA in 2018 for SGI (to the left) and LGI (to the right) [19]. CGI data is included in the LGI data, as the primary application for CGI is cylinder blocks and heads.

After the short panic the COVID-19 pandemic created, things appear to run again following the same steps as before. In particular, there is no more any question on the fact that the demand for goods transportation must be met, which led to the development of gigantic cargos that require corresponding engines (Fig. 9). These engines are run with high-sulphur oils that pollute air to an incredible level, but significant development is ongoing in this field as well, with low-sulphur fuel mandated since 2020, longer-stroke engines that provide efficiency improvements by reducing rpm, and the likely introduction of ammonia as an alternate fuel in the near-term. Stronger cast irons are required to ensure that this demand can be satisfied with more efficient engines and with decreased pollution.

In the introduction, we abruptly stated that cast irons are 'green' materials with respect to others cast alloys (cf. Fig. 1). This is certainly not all the truth. Similar to other engineering materials, the production of cast irons has steadily increased since the 19th century, with the associated increase of environment impacts (pollution, energy and primary resource consumption, green-house gas -mostly CO_2-emissions, ...) to reach an overall level that has become unacceptable. However, sustained efforts have long been made to decrease pollution from fumes during melt preparation (both blast furnaces and other foundry furnaces). Because the cupola will be banned in Europe in 2050, the full

circle – from only blast furnaces and cupolas to only electric – will be closed in about two centuries.

Figure 9. A large ship engine (Wärtsilä X62 engine), the steps on the left side can be used for an estimate of the scale. (https://www.wartsila.com/media/news/08-01-2015-wartsila-x62-engine-now-fully-approved-and-available-to-the-market

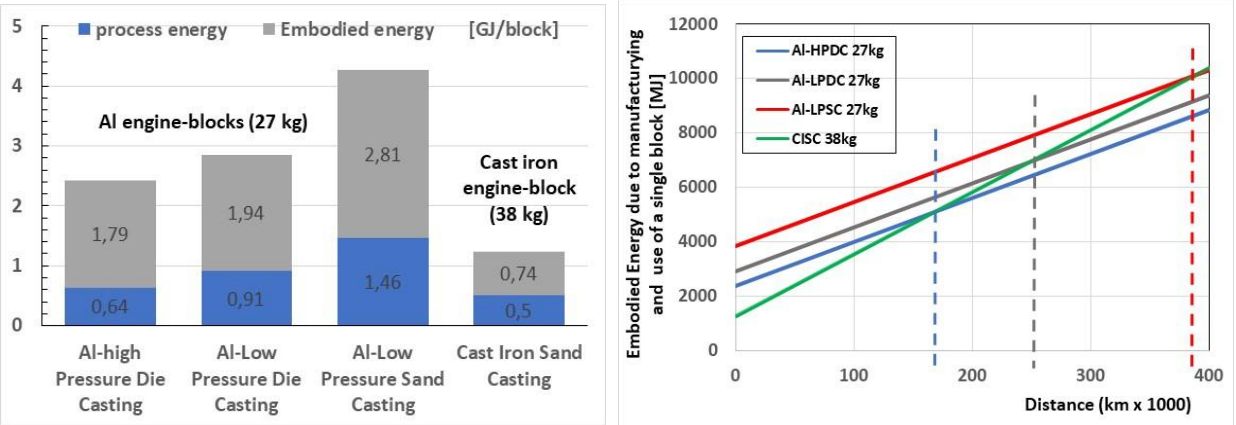
More recently, fine and complete life cycle analyses (LCA) have been carried out, which trace the environment impacts at different steps of the whole extraction and production process (see for instance [20-24] and an example in Fig. 10). These tedious works are necessary guides for still reducing energy consumption and CO_2 footprint of casting industry. Recyclability is also a positive point for cast irons. The percentage of recycled and downcycled material in the total worldwide supply of grey cast irons has reached about 70%, compared to less than 50% for cast steels or Al-alloys [2]. Finally, a particular feature of aluminium and cast iron castings is the use of huge amounts of sand, with green sands that may be recycled while sands that have been chemically bound cannot. It is noted that the gravity sand casting of passenger vehicle aluminium cylinder blocks uses approximately four times more chemically bonded sand than an equivalent cast iron cylinder block.

Stronger materials, like CGI, also reduce the weight of conventional LGI components, contributing to the environment by reducing the melting demand. If CGI reduces the weight of a grey iron cylinder block by 15%, the saving corresponds to 7,500 tonnes per year of castings and 10,000 tonnes per year of liquid metal for every one million 50 kg cylinder blocks. In turn, this saving corresponds to a reduction of 100 MJ of energy for electric melting and 500 tonnes of CO_2 per year.

In transportation industry, the weakest point of cast irons is clearly their high density, which evidently suggests to substitute them by lighter materials, as Al-alloys or even Mg alloys. However, this solution needs to be validated for each component, since the gain in energy consumed (or CO_2 generated) during service can not always counterbalance the excess of energy used for the production of lighter alloy (cf. Fig. 1 and Fig. 10-a). As an example, Fig. 10-b (from [23]) shows that the break-even distance for paying back the substitution of cast iron by Al-alloy in a given engine block is of the similar or even longer than the service life of the vehicle.

While considerable attention is given to the electrification of passenger vehicles, the market penetration to date – and the likely development over the next decade – is not as rapid as most media reports suggest. The pie charts to the right of Fig. 11 show passenger

car sales in 2020 for Europe, the US and China according to fuel, namely petrol, diesel, hybrid, electrified (plug-in hybrids plus battery electric vehicles) and alternate fuel (propane, natural gas, etc). Globally, passenger vehicle electrification in 2020 was less than 10% and, as shown in Fig. 11, global sales are expected to be approximately 30% in 2030. Many of these vehicles will be hybrids, also containing an internal combustion engine. On the commercial vehicle side, there is no foreseeable alternative to the diesel engine for long-haul heavy duty goods transport and there is a widespread consensus in the industry that the diesel engine will dominate until at least 2040. Even if the transformation to electrification becomes complete, the internal combustion engine will remain on global road for decades after production stops. Clearly, there is a need for continued research in cast iron to make the internal combustion as environmentally effective as possible.



a b

Figure 10. a) Energy for manufacturing a 1.6 L diesel engine block made of cast iron (38 kg) or Al alloy (27 kg); b) Total (manufacturing + use) energy as a function of driving distance for the same engine block in an automotive vehicle of 1200 kg with an average consumption of 7 L/100 km; vertical dotted lines mark break-even distances between cast iron and Al-alloy produced by different casting processes; the average life of such a vehicle is approximately 220 000 km. (adapted from [23]).

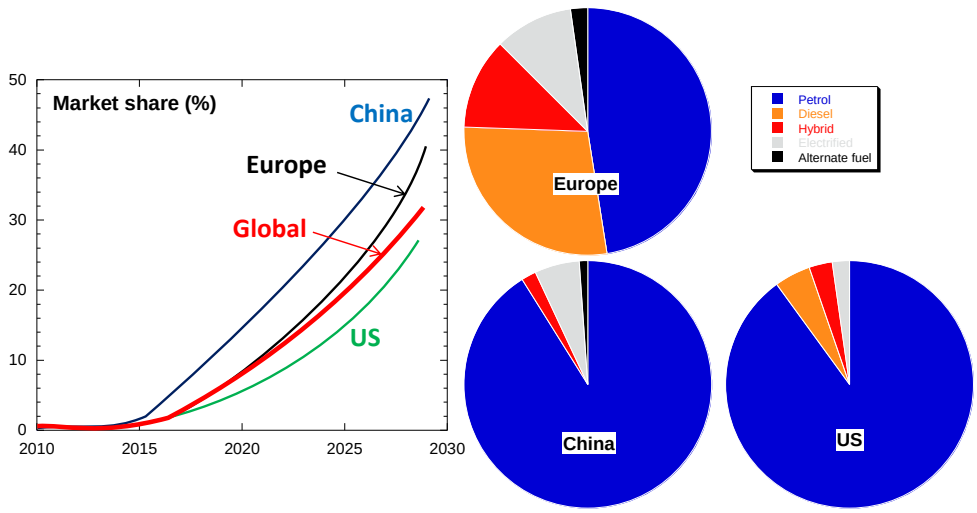


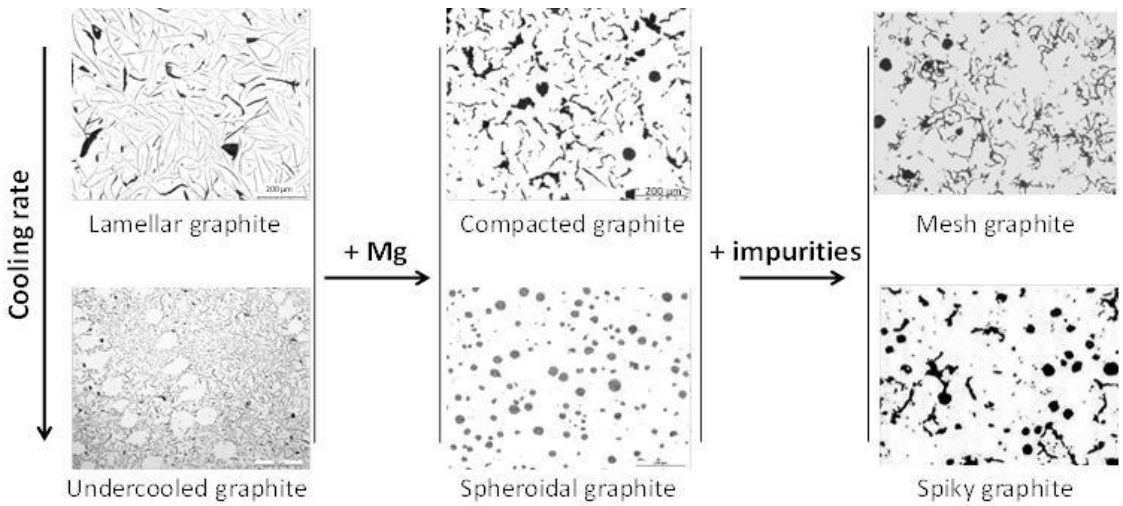
Figure 11. Penetration of electrically charged vehicles is poised to remain below 50% for at least the next decade (adapted from Automotive News, 17 May 2021). The pie charts show passenger car sales in 2020 for Europe, the US and China according to fuel.

5. Future outlooks: a material worthy of further research

At the end of the 20th century, progress in metallurgy has benefited from the development of computers and small-scale analytical methods. Computer capabilities have been first used for developing simulation tools for describing the successive processes of melt preparation, filling and casting, and several commercial software packages are nowadays available. Another important application is in the control of melt preparation just before pouring that makes use of thermal analysis with dedicated rapid curve analysis so that a green or red light is provided prior to casting, enabling the foundry to adjust the iron and to ensure that only good iron is poured. However, the most exciting advances for metallurgists are the capabilities of modern apparatus to investigate matter at small-scale, going down to atom scale as with the so-called Atomic Resolution Microscopes. This certainly opens ways to improve the understanding of microstructure formation in cast irons.

In general, it is desirable for lowering the costs to use cast iron parts in their as-cast state, which means avoiding heat-treatments. This implies that the graphite shape and the matrix constitution that were sought for are obtained, which may be challenging in parts having complex shapes. As a matter of fact, the shape of graphite is highly sensitive to small changes in both melt preparation and cooling rate. Furthermore, changes brought about by these factors are closely inter-related; see Fig. 12. After standard preparation, a cast iron melt yields flake graphite, while a full or partial spheroidizing treatment after desulphurisation is used to get spheroidal or compacted graphite, respectively. However, in a casting with various section thicknesses, the graphite shape depends on the local cooling rate. The following changes can be noticed as the cooling rate increases:

- Lamellar graphite to undercooled graphite.
- Compacted graphite with low nodularity to nearly or fully spheroidal graphite.
- Irregular spheroidal graphite to well-rounded one.



- **Figure 12** The interplay between chemical and cooling rate routes (after [28]).

Inoculation helps controlling graphite shape, e.g. avoiding undercooled graphite in LGI that would conduct to a ferritic matrix while fully pearlitic LGI are preferred for mechanical properties. Furthermore, obtaining a fully graphitic SGI upon casting definitely relies on appropriate inoculation of the melt for avoiding the formation of metastable eutectic. Understanding the bases of the formation of graphite nuclei [25, 26] has allowed

defining new inoculant compositions in particular to fight against fading and thus against porosity in SGI. This is an area of fierce competition on an industrial point of view, and of sharp stimulation for scientists. The main concern is understanding early precipitation and growth of graphite, in particular in relation with the presence of additives in the inoculants. Recent results on hypereutectic alloys strongly suggest that both primary and eutectic growth of graphite needs a significant undercooling to proceed, and that this undercooling depends on melt chemistry [27]. This should lead to revisit thermal analysis records as well as modelling approach of cast iron solidification.

The additives mentioned above are elements prone to react with oxygen, sulphur and nitrogen to precipitate compounds that are active in the process on graphite nuclei formation. However, at the same time, many of these elements also affect graphite shape and are then seen as impurities leading to graphite "degeneracy" - i.e. the development of unwanted graphite forms – when present in the melt at a level above a critical limit that may be so low that these so-called poisoning elements can often be classified as trace elements. These degeneracies are illustrated in Fig. 12 with mesh and spiky graphite in the case of SGI, but the phenomenon is also known for LGI and CGI. While the role of these impurities have been described since a long time as can be seen in several reviews [29, 30], understanding how they actually proceed to induce graphite degeneracy is still in its infancy [31]. In practice, rare earths are used to fight the deleterious effects of trace elements, but again very little has yet been made to describe the kinetics of the very many precipitation and dissolution processes behind rare earths additions [32, 33].

The precise mechanism of the action of the spheroidizers is still unknown, or more precisely, still controversial. The first effect of magnesium and rare earths has long been associated to their high affinity with oxygen and sulphur, i.e. considering that change in graphite shape is controlled by tightening oxygen and sulphur as oxy-sulphides. Subramanian et al. [34] therefore suggested associating the different forms of graphite with the thermodynamic activity of residual oxygen and sulphur. The presence of some residual magnesium and RE dissolved in the liquid of a melt dedicated to SGI and CGI appears however essential for achieving the desired graphite shape with the associated challenge of understanding the exact way these elements interact with graphite.

In the same way as for graphite shape, the constitution of the matrix in the as-cast state depends both on the chemical composition and on the cooling rate, with a strong effect of graphite fineness. Increased inoculation in SGI and decrease of graphite size in LGI eases the transformation of the matrix in the stable system, i.e., increases the amount of ferrite. On the other hand, increased cooling rate favours the transformation in the metastable system with precipitation of pearlite. Adding Sn and Sb is used industrially to avoid the formation of ferrite, with the risk of graphite degeneracy if added at too high levels. It is thus usual to add also Mn and Cu which are less potent for pearlite formation but are also easier to tolerate when considering the avoidance of deleterious graphite shapes. An important feature of the eutectoid transformation is the effect of microsegregations that are issued from the solidification step. While they can be easily described [35], their mastering for controlling the eutectoid transformation has not yet given the expected results. Microsegregation is also a concern for achieving controlled austempering of ADI parts as well as for mastering so-called dual-phase microstructures. Here, it is worth noting that recent works have demonstrated that 1-3 wt.% Al added to a silicon cast iron inverses silicon segregation [36, 37]. This finding may soon be exploited to decrease microsegregation and thus improve matrix properties of cast irons.

Improvements of melt and casting processes as well as mastering of microstructure formation are triggered by the need for better service properties within a framework of competition between materials. For dynamic properties, and in particular in the case of SGI, it is not only the matrix constitution that is important but also the casting defects such as porosity. Some progress has been made in describing porosity formation [38] though still not accounting for the mechanical effect due to graphite bulging that has long been recognized but has rarely been accounted for [LES09]. Also, the mechanical behaviour of cast iron is intrinsically elasto-visco-plastic with a strong effect of damage which has led to a wealth of complex modelling approaches that are hardly introduced in foundry software packages. Ad hoc models fitted to experimental overall mechanical behaviours are often preferred.

Beyond the metallurgy itself, significant improvements continue to be introduced to the mechanical engineering side of the foundry. Over the last 25 years, complex components like cylinder blocks and heads have progressively evolved from green sand casting to fully-enclosed core packages. In parallel, minimum wall thickness for passenger vehicle cylinder blocks has decreased from 4.5 mm (+/- 1.0 mm) to the current state-of-the-art of 2.7 mm (+/- 0.5 mm). And the development has not stopped. Until recently, 3D sand printing was preserved for rapid prototyping, but many series production foundries are now embracing additive manufacturing for the production of highly complex cores. Without draft angles, these complex cores can add to weight reduction and eliminate costly – and energy consuming – post processing of the castings.

6. Conclusion

We continue to judge the iron foundry by its grey walls, despite the significant progress in cleaning up the dust. The real image should be the atoms, not the walls. Cast iron is the first composite material, and it remains one of the most versatile composites available today from a technical point of view, and one of the most fascinating from a scientific point of view. In the future, iron foundries will produce castings with different graphite shapes in different areas of the component to optimise specific properties where they are needed. While the iron foundry world may struggle for image, our present-day ability to control alloy additions to within 10 grams per tonne will soon seem rudimentary. The real iron-age is just beginning and the next iron will build its own legend.

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