

Heat Treatment Technology

Malleable Irons MCI

White & Black Heart MCI

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What are malleable irons

- **Malleable iron** is a cast ferrous metal that is initially produced as **white cast iron**, then is heat treated at high temperatures (**950–1050 °C**) for relatively long time (**75 and 100 h**) to convert the carbon-containing phase from **iron carbide** to a nodular form of graphite usually called **temper carbon**.
- There are two types of malleable iron, **black heart**, and **white heart malleable cast irons**.

Introduction to Malleablizing heat treatment

- **The main advantage of cast irons** is the possibility of obtaining near-shape parts by moulding, without forging after solidification.
 - **The term malleable** refers to the possibility of conferring more deformability to the cast irons through heat treatment in solid state.
 - **Two kinds of ferritic malleable irons** will be described in this lecture, **white and black heart malleable cast irons**.
1. Malleablizing treatment **in white heart** malleable cast irons is based on the decomposition of the cementite into iron and carbon atoms (temper carbon), diffusing then the carbon towards the periphery where **it oxidizes**, being **modified the chemical composition** of the initial white cast iron.
 2. **In the case of black heart malleable cast irons**, the chemical composition of **the original white cast iron is not modified**, and cementite is decomposed into carbon, which transforms into nodular graphite (nodular form of graphite usually called **temper carbon**), and austenite, which allows obtaining either **pearlitic or ferritic matrix depending on the cooling conditions after its transformation**.

White Heart Malleable Cast Iron

White Heart Malleable Cast Iron

- The malleablizing process is mainly an oxidizing annealing (Fig. 6.1). Before the heat treatment, white cast iron parts are usually packed up in boxes with a material that provides oxygen, such as iron oxide. Afterwards, parts are heated at a temperature of **950–1050 °C** and then are held between **75 and 100 h**. **This is to ensure that all cementite splits up into carbon and iron atoms**.
- Simultaneously, decarburizing the austenite is also expected, which at the heat treatment temperature can have between **1.4 and 1.7 wt.% C in solid solution**.

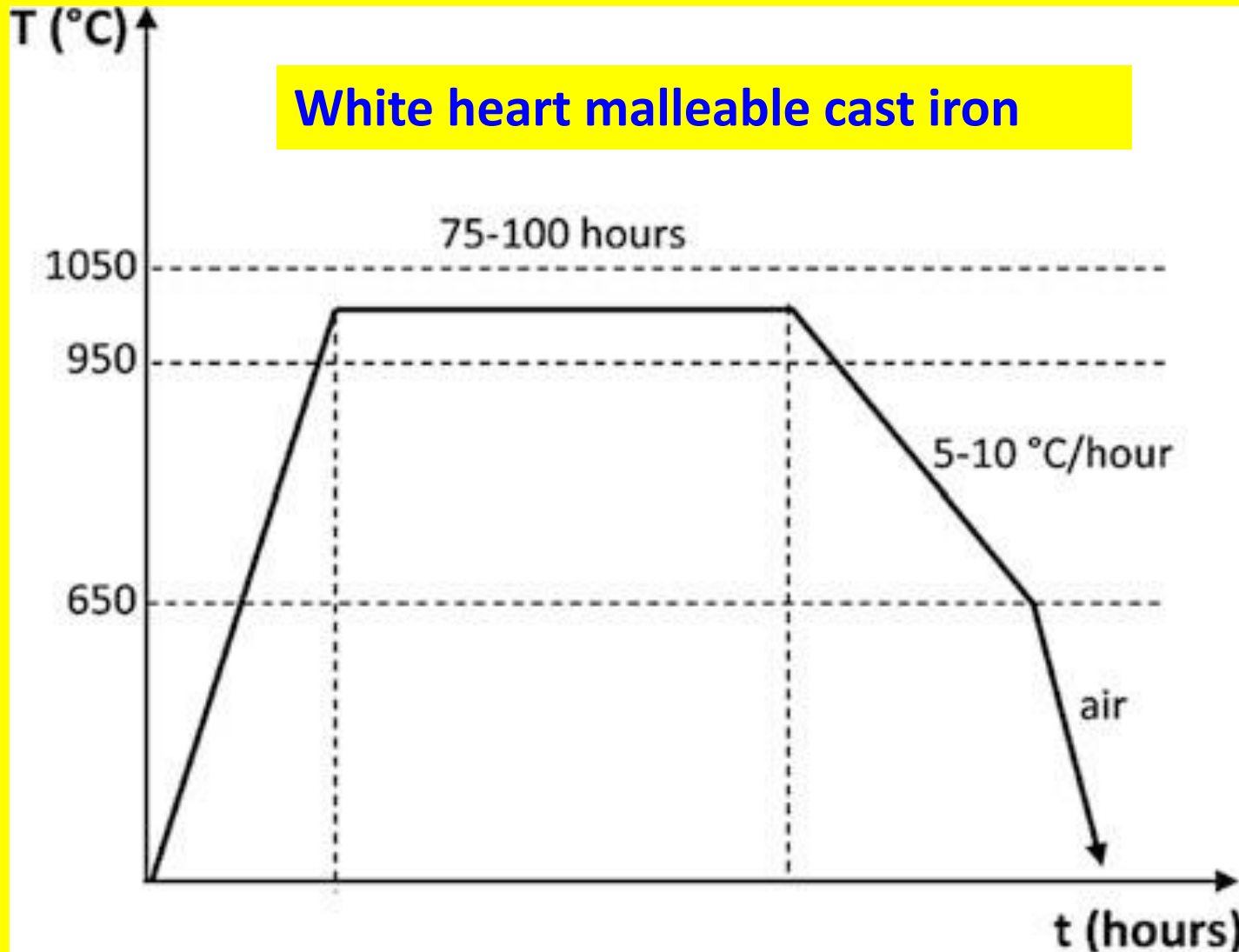
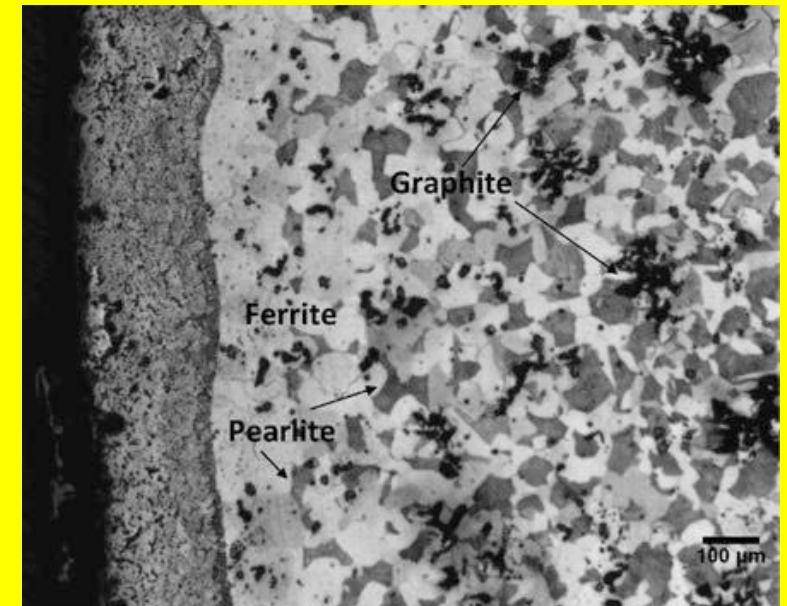


Fig. 6.1 Heat treatment cycle used for obtaining

Oxidizing annealing (First Stage Graphitization)

Simultaneously, decarburizing the austenite (1.4 and 1.7 wt.% C in solid solution).



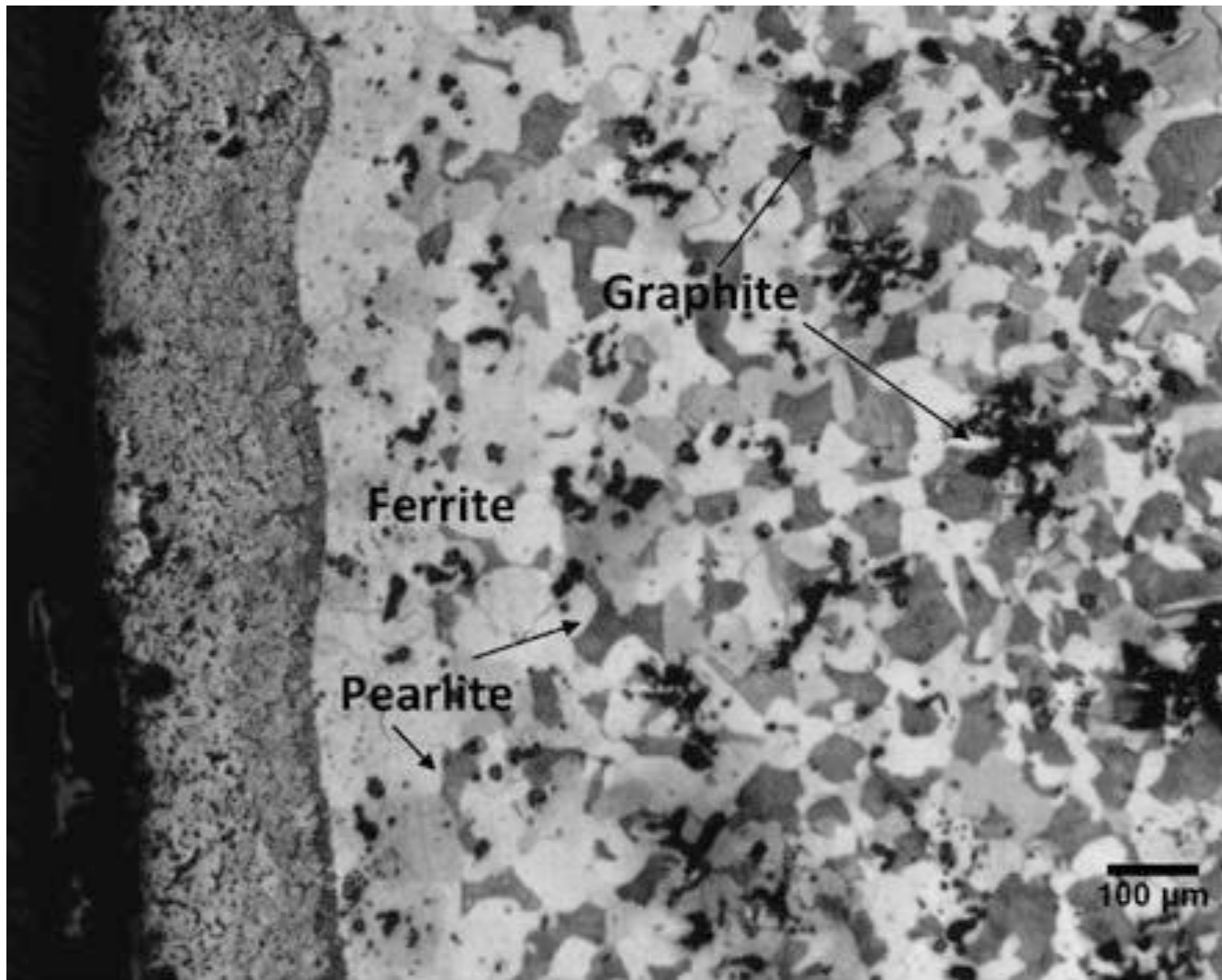


Fig. 6.2 White heart malleable cast iron. The malleablizing treatment was based on a heating up to 1060 °C in 8 h; holding at that temperature for 80 h; and cooling down to room temperature in 12 h.

- **The total duration of the treatment is** normally around 6 days:
- one for heating, three of maintenance at high temperature and two days of cooling from the high temperature down to 650 °C

Cementite \rightarrow Graphite (temper carbon) + Fe FSG at 950 1050 °C
Cementite + O₂ \rightarrow CO₂ + Fe (with C in solid solution) at 950 1050 °C
Austenite + O₂ \rightarrow CO₂ + Fe (with C in solid solution) at 950 1050 °C

- **Not every carbon dissolved in gamma iron reach the surface** of the part by diffusion, and for that reason, from this temperature down to temperatures lower than the eutectoid, **the cooling should be very slow (from 5 to 10 °C per hour).**
- **If the part is cooled like this down to 650 °C**, the carbon migration towards the part surfaces will favour its conversion into CO₂, and specially, **the formation of pro-eutectoid and eutectoid (pearlitic) cementite is avoided.** Under these conditions, the outside of the part, with decarburized austenite, will easily transform into ferrite, even in metastable cooling.
- However, **the inner zones of the part**, whose austenite did not eliminate all its carbon, would produce pearlite.

The composition of the original white cast iron.

- The composition of the original **white cast iron must be hypoeutectic**. That is because less carbon should be removed. The common percentages of this element range within 2.9 and 3.3%. Lower values would compromise the castability.
- **Silicon** improves this property (castability) and favours the decomposition of the cementite. However, **silicon content should be restricted** with the purpose of avoiding the possibility of a stable solidification (grey or mottled iron). Habitually, silicon ranges **within 0.45 and 0.75%**.
- The same happens with **sulphur content** that **should be low (maximum 0.20%)**, to avoid the formation of **FeS–Fe eutectic** that would melt down during the heat treatment.
- **Manganese** must compensate sulphur (**1.72% S + 0.15%**) with the purpose of achieving the combination of manganese with sulphur to obtain MnS.
- **Phosphorus** content should be also low. The maximum percentage of phosphorus should be **lower than 0.15%** to avoid the formation of **steadite** that also would melt down at the heat treatment temperatures.
- **Steadite**: A hard structural constituent of cast iron consisting of the eutectic of ferrite and iron phosphide (Fe_3P); composition of the eutectic is 10.2% phosphorus and 89.8% iron; melts at 1049°C

Mechanical properties & application of the white heart malleable cast iron

- The following values are representatives of **the mechanical properties of the white heart malleable cast iron**: **350 MPa** of tensile strength (higher than the one of a ferrite without silicon), **5–15% of elongation** (in very thick walls an elongation of 25% could be achieved) and **Brinell hardness of 150 HB**.
- **White heart malleable cast iron is used in parts of small thickness and complex shapes** whose manufacture by means of solidification would result advantageous in comparison with forming through forging. Nowadays, sintered alloys compete advantageously with the white heart malleable cast irons for a lot of applications.

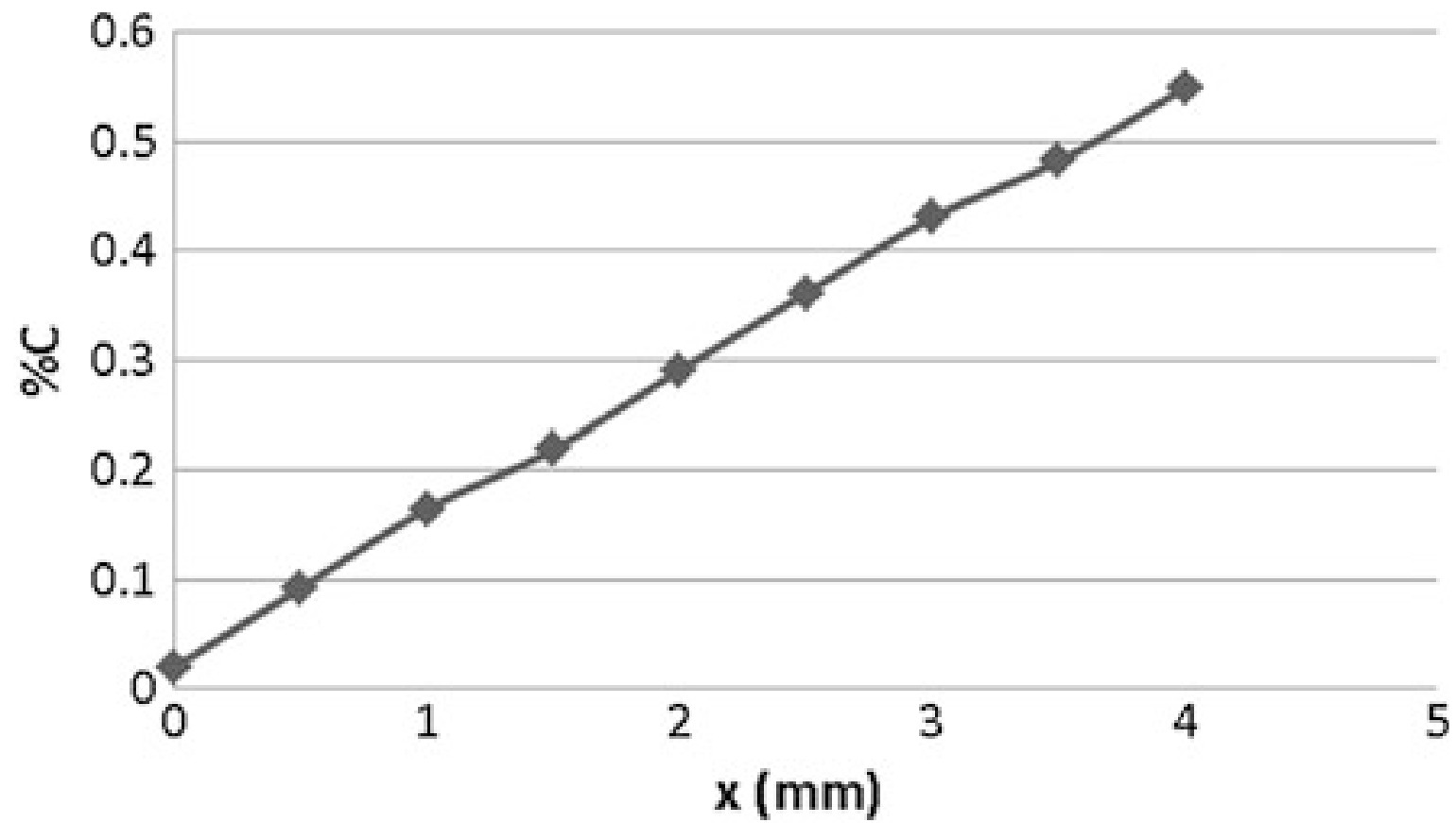


Fig. 6.4 Representation of the $\%C$ as a function of the distance x

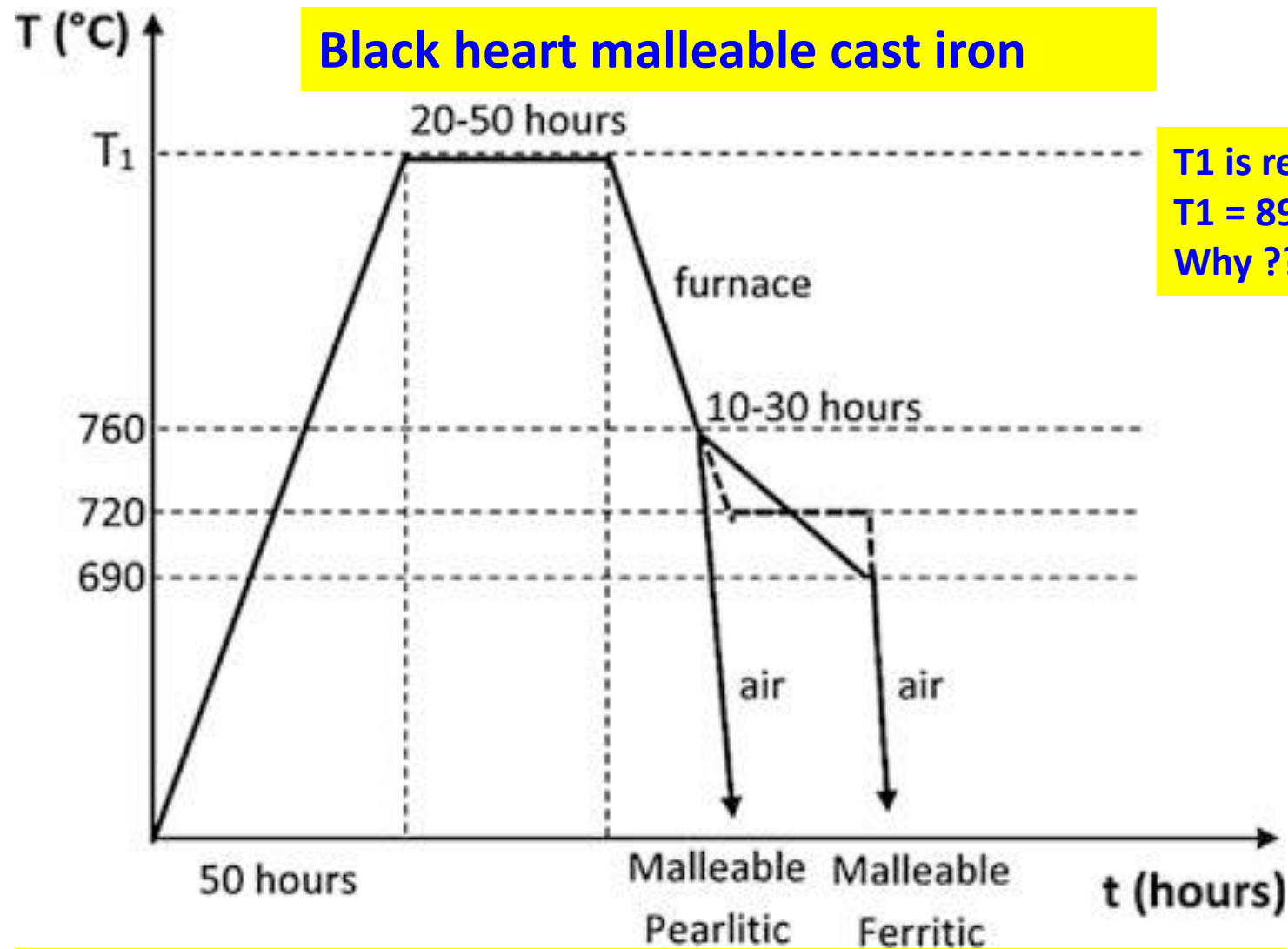
Blackheart Malleable Cast Iron

Blackheart Malleable Cast Iron

- The heat treatment for malleablizing a white cast iron by means of transformation of cementite into graphite, **without modifying the chemical composition of the cast iron**, provides a metallic material that is usually known as blackheart malleable cast iron. This process that is used in the malleabilization of cast irons was first employed in USA, in Newark, in 1830.
- The heat treatment is performed in **neutral atmosphere**, or in **controlled atmosphere**, **to avoid that** the carbon that was obtained from the cementite decomposition was oxidized again. Exactly, the opposite to what happens when a white heart malleable cast iron is manufactured.

- The heat treatment is performed in **neutral atmosphere, or in controlled** atmosphere, to avoid that the carbon that was obtained from the cementite decomposition was oxidized again. Exactly, the opposite to what happens when a white heart malleable cast iron is manufactured.
- In this case, the chemical composition of the original white cast iron is not modified, and the chemical reactions for the malleabilization, in austenitic state, at temperatures **T1 of 890–950 °C**, are mentioned below:
 - **Fe₃C → graphite + austenite** (with the% carbon corresponding at T1)
 - **Austenite → graphite + austenite** (with the% carbon corresponding at T1)
- Graphitization could be achieved in **lower times at temperatures (T1) higher than 950 °C**, but **graphite would grow as lamellar**, and **this kind of graphite is unfavourable for toughness**. With temperatures in the range 850–950 °C nodular morphologies are obtained. These morphologies give **good toughness**.
- **The time at** the temperature T1 lasts between **20 and 50 h depending on** the carbon content of the white cast iron part. The lower the carbon content and the higher the silicon content (it should be remembered that is a graphitizing element), the lower the heat treatment duration.
- **Silicon and carbon usually** keep the next relation: **3.5% < C% + Si% < 3.9%**

- **Silicon percentages range** between **1.25 and 1.55%**.
- **Sulphur, manganese and phosphorus** percentages are those that were mentioned in the white heart malleable cast iron situation.
- **The carbon content** is lower in blackheart malleable cast irons than in the white heart malleable cast irons. In the first one cementite transforms into graphite. For that reason, the mechanical properties (tensile strength, elongation), as happens in grey cast irons, are better when the graphite content diminishes. Carbon content is commonly comprised **within 2.1 and 2.8%**. These values advise us to obtain the cast iron in an electric furnace. In cupola furnaces, achieving carbon contents lower than 2.8% is complicated because the cast iron easily absorbs carbon because of the contact between the liquid cast iron and the coke.
- **The heat treatment cycle** for achieving a blackheart malleable cast iron is represented in Fig. 6.5: **50 h in heating, from the room temperature up to the temperature T₁**; between **20 and 50 h of holding time at T₁**—**lower time and for that reason cheaper than obtaining the white heart malleable cast iron**—; and **different cooling rates depending on** the required matrix, although, in any case, **the cooling down to 760 °C is** done as fast as the thermal inertia of the furnace allows.



Black heart malleable cast iron

T_1 is relatively lower than in the case of white heart.
 $T_1 = 890-950^{\circ}\text{C}$
 Why ???

Fig. 6.5 Heat treatment cycle used for obtaining blackheart malleable cast iron

Ferritic Blackheart Malleable Cast Iron

- Achieving a thoroughly ferritic matrix requires a **very slow cooling** down to temperatures below the eutectoid. The reason is that transformations **will follow the Fe–C stable diagram**.
- **Descending from 760 to 690 °C should take between 10 and 30 h.** This slow cooling is sometimes replaced, with the purpose of diminishing the operation time, by an **isothermal holding at 720 °C that is called second graphitization.** **The first graphitization would be that performed at 890–950 °C.** Once obtained a ferritic matrix, parts are air cooled.
- The blackheart malleable cast iron, of ferritic matrix, Fig. 4.7, has a tensile strength between **250 and 375 MPa**, yield strength between **160 and 250 Mpa** (lamellar grey cast irons do not have yield strength) see Fig. 6.6, and **elongation that can even reach 25%.** Nevertheless, in the worst situation, elongation is higher than in the grey cast irons situation.
- Ferritic blackheart malleable cast iron is **used in the automotive industry, expansion joints in bridges, pressure valves, etc.**

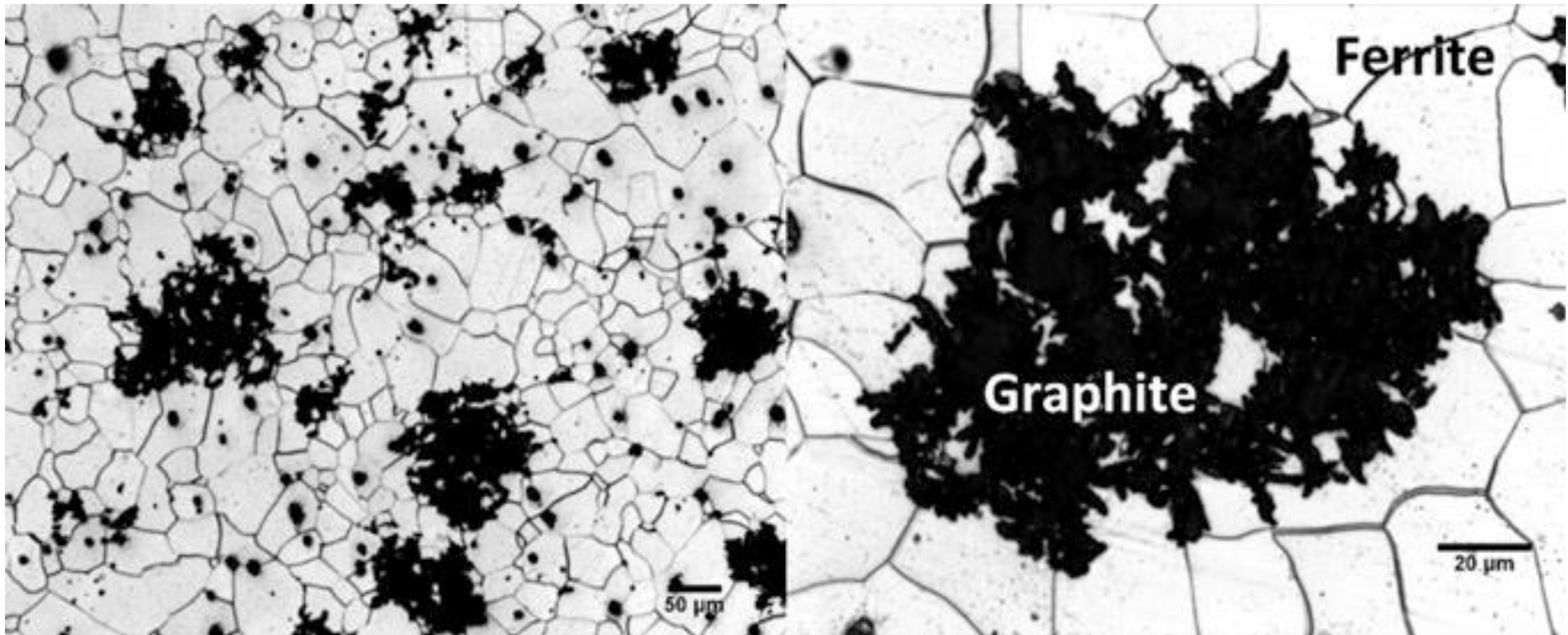


Fig. 4.7 Blackheart malleable cast iron of ferritic matrix (nodular graphite over background of ferrite). Etched with Nital 2

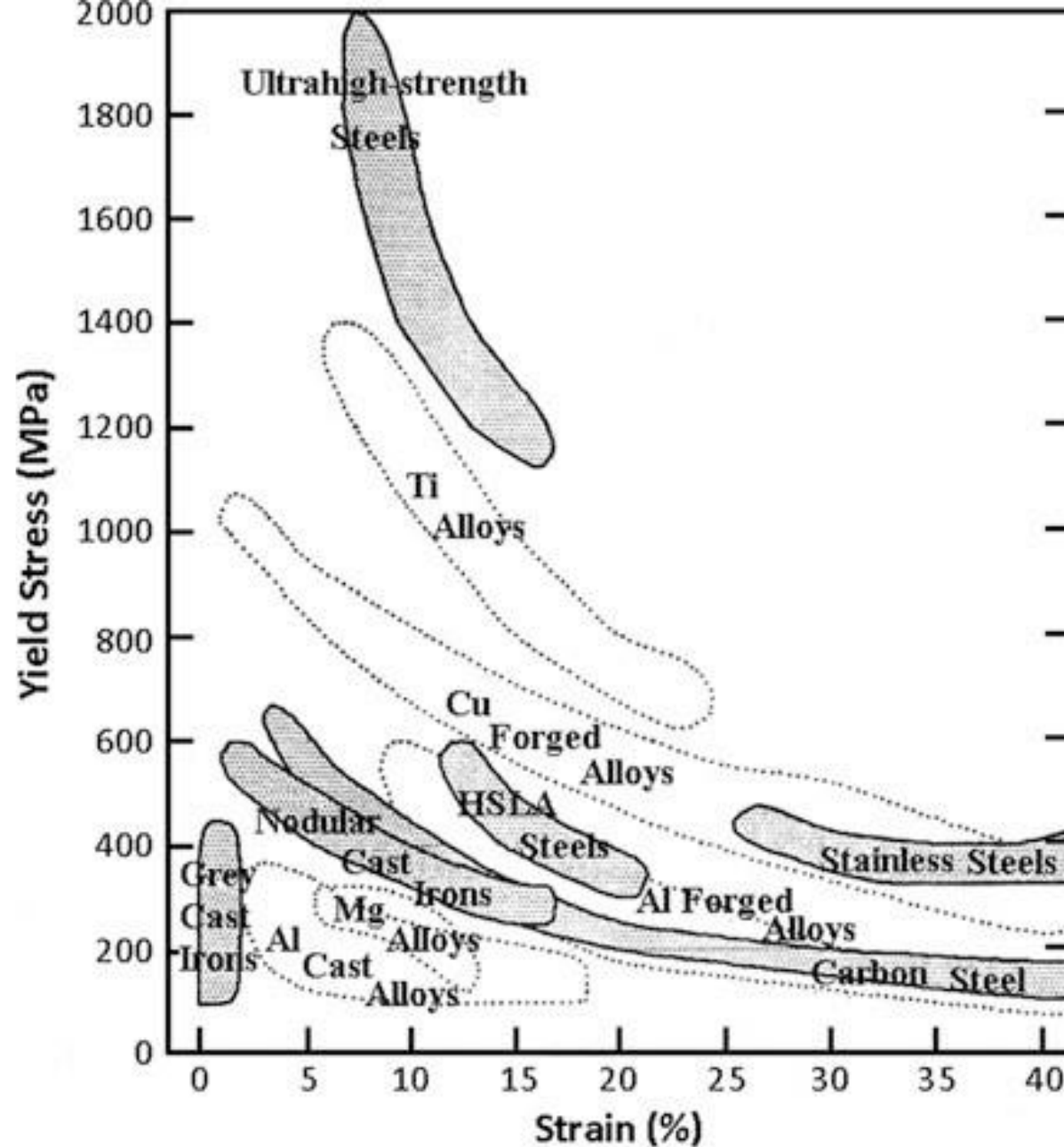


Fig. 6.6 As opposed to other materials, lamellar grey cast irons do not have yield strength

- **Ferritic malleable** cast irons are susceptible of heat treatment. In this way, by means of austenization at 840–870 °C, and subsequent air cooling it is possible **to achieve a pearlitic matrix**.
- **The tensile strength would be of 550 MPa and the elongation of 3–4%.**
- This possibility of heat treatment also justifies the use of a **case-hardening** which transform the matrix constituent into martensite.

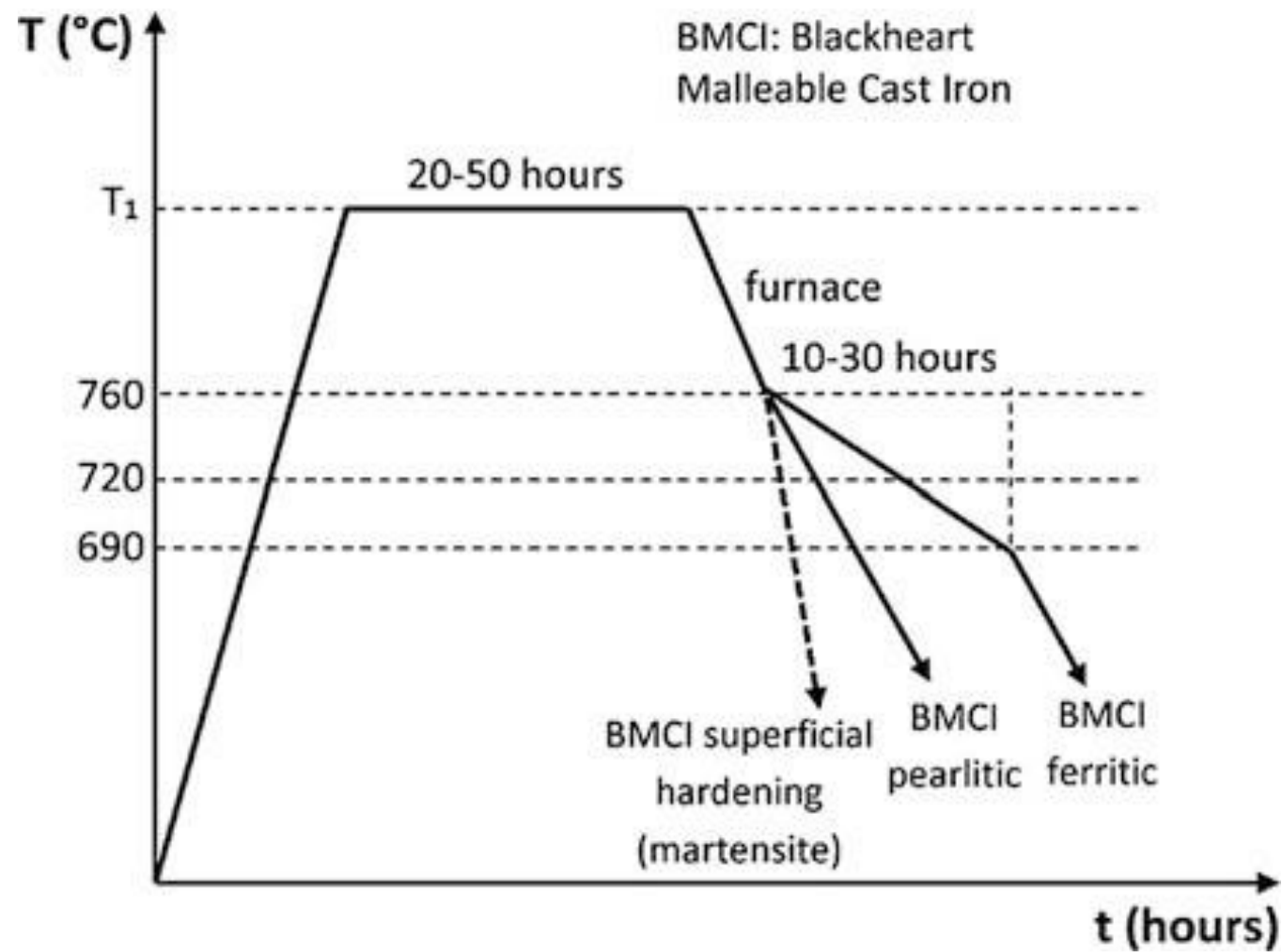


Fig. 6.8 Structures that can be obtained in a blackheart malleable cast iron

Blackheart Malleable Cast Iron of Pearlitic Matrix

Blackheart Malleable Cast Iron of Pearlitic Matrix

- The pearlitic matrix can be directly obtained after the first-stage malleabilization treatment. **Simply by air cooling from the temperature of 760–780 °C, the eutectoid austenite will transform into pearlite, by following the Fe–C metastable diagram.**
- **When the cooling between** the temperature T1 and 760–780 °C is **very slow**, then unfavourable areas of ferrite can appear, because of the direct ferritization, in the boundaries of the nodular graphite (Fig. 6.7).
- The properties of the blackheart malleable cast irons of pearlitic matrix and the ones of ferritic matrix are related between them, as the pearlitic and the ferritic steels properties are related between them.

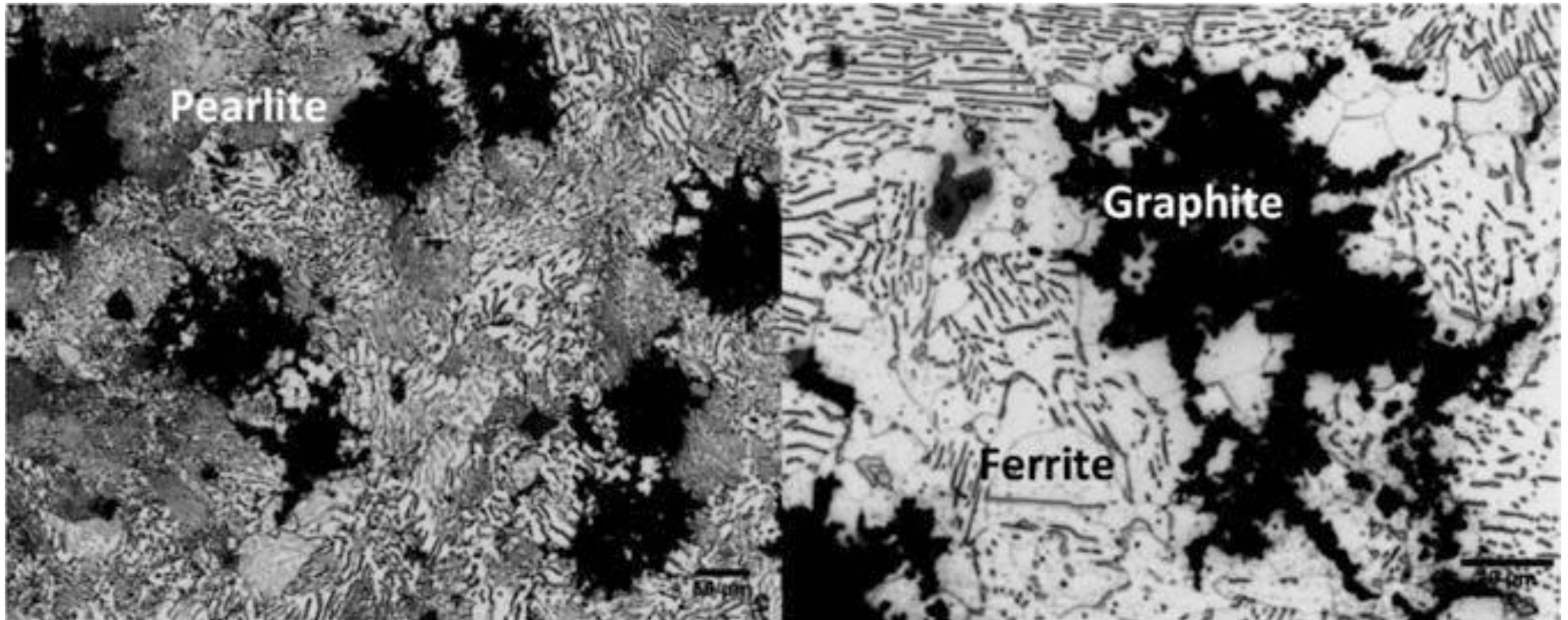


Fig. 6.7 Blackheart malleable cast iron (Nital 2 etched).

- a. Pearlite matrix
- b. (Pearlite –Ferrite) Direct ferritization areas between the nodular graphite and the pearlite

- **Pearlitic cast irons** have more tensile strength than the ferritic cast irons— R_m of the pearlitic, between **400 and 600 MPa**—also more hardness and lower ductility. (R_m Ultimate compressive strength, R_p yield strength, FS fracture strength).
- **Their elongation** is usually between **10 and 2%**. But, as opposed to the ferritic blackheart cast irons, R_m and elongation (%) evolve in the contrary direction as happens in steels (R_m diminishes when elongation grows).
- **Pearlitic cast irons** have a **good damping capacity** (damping capacity is the ability of a material to quell (absorb) vibrations and to dissipate the energy as heat, or simply the relative ability to stop vibrations or ringing; or can be also defined as the internal energy dissipation at large stresses and strains). By the contrary, these cast irons have **a lower machinability** than the ferritic cast irons. Pearlitic cast irons have an **excellent wear resistance** and provide a suitable behaviour to alternating stresses that could produce fatigue.

- **The pearlitic blackheart** malleable cast iron can be thermally treated. For instance, after the first malleabilization annealing, it can be oil-quenched. The times required for martensite (formed during the oil-quenching) tempering are usually of 2 h, or even more, to achieve microstructure uniformity. The globulization of cementite in a pearlitic cast iron is also possible by means of a subcritical annealing.
- These structures of globular pearlite, which are obtained with lower costs, compete in their applications with the structures of tempered martensite. Obvious (for obtaining nodular graphite) justify the large field of industrial applications.

- These cast irons are usually competitive with steels in some parts of agricultural vehicles, railway elements and some automotive components (gear assemblies, connecting rods, pistons, camshafts and generally complex shape parts) that are advantageously obtained through casting, which is cheaper than forming (forging) usually required for steel components.
- White heart malleable cast irons cannot be used in broadly applications. That is consequence of the thickness limitations, the difficulty for being manufactured by mass production, the expensiveness of the malleabilization (due to the time-consuming heat treatment) and the lower mechanical strength.
- The great series of blackheart malleable cast irons usually have not thicknesses higher than 40 mm. However, great quantity of parts until 100 mm thickness and 150 kg weight are also produced. Malleable cast iron parts advantageously compete with sintered parts.

Shortening of malleablizing heat treatment time

Shortening of malleablizing heat treatment time (**by alloying with modifier or inculcated elements** and/or by introducing internal **stresses**)

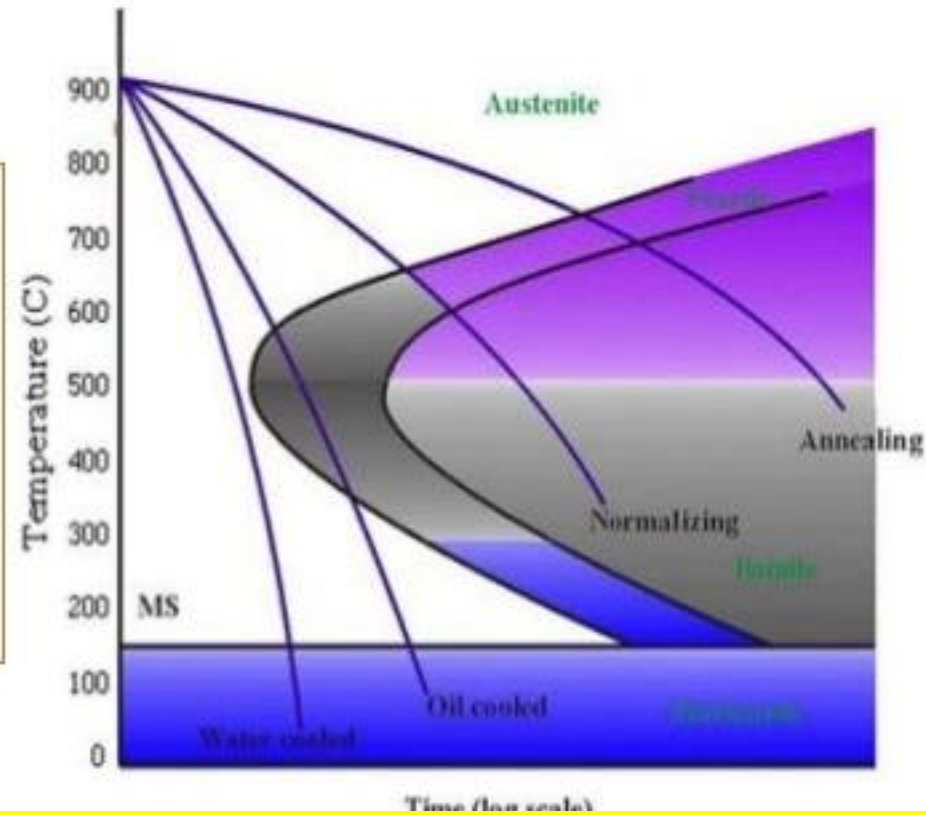
- CONCLUSIONS Cu, Ni, Mo

1. With the increase of malleablizing time, the eutectic carbide content is reduced while the retained austenite content increases. Moreover, **1 wt pct copper** addition is effective in eliminating all eutectic carbides **after 930 C–20 hours** malleablizing and promotes the formation of retained austenite in the matrix.
2. The malleablizing time can be shortened **by adding internal stresses** that can become graphitization centres by quenching.

Some related important information

The Temperature Transformation (TTT) Diagram:

- Depending on the type of heat treatment, time and temperature, final microstructure of the steel, or any Iron carbon will be changed and so does the properties.



The effect of cooling on the structure and properties.

Material	Brinell Hardness Number - HB
Lead	5.0
Pure Aluminium	15
Copper	35
Soft brass	60
Hardened Aluminium	75
Mild steel	130
Annealed chissel steel	235
White cast iron	415
Nitrided surface	750
Glass	1550
Rhenium diboride	4600

Material	Yield Strength [MPa]	UTS [MPa]
Aluminum	35	90
Copper	69	200
Brass	75	300
Iron	130	262
Nickel	138	480
Steel	180	380
Titanium	450	520
Molybdenum	565	655
Zirconium alloy (typical cladding)	380	510
08Kh18N10T stainless steel	216	530
Alloy 304L stainless steel	241	586
SA-508 Gr.3 Cl.2 (low- alloy ferritic steel)	500	700
15Kh2NMFA (low-alloy ferritic steel)	490	610

Mechanical properties of some metallic alloys and some other materials.

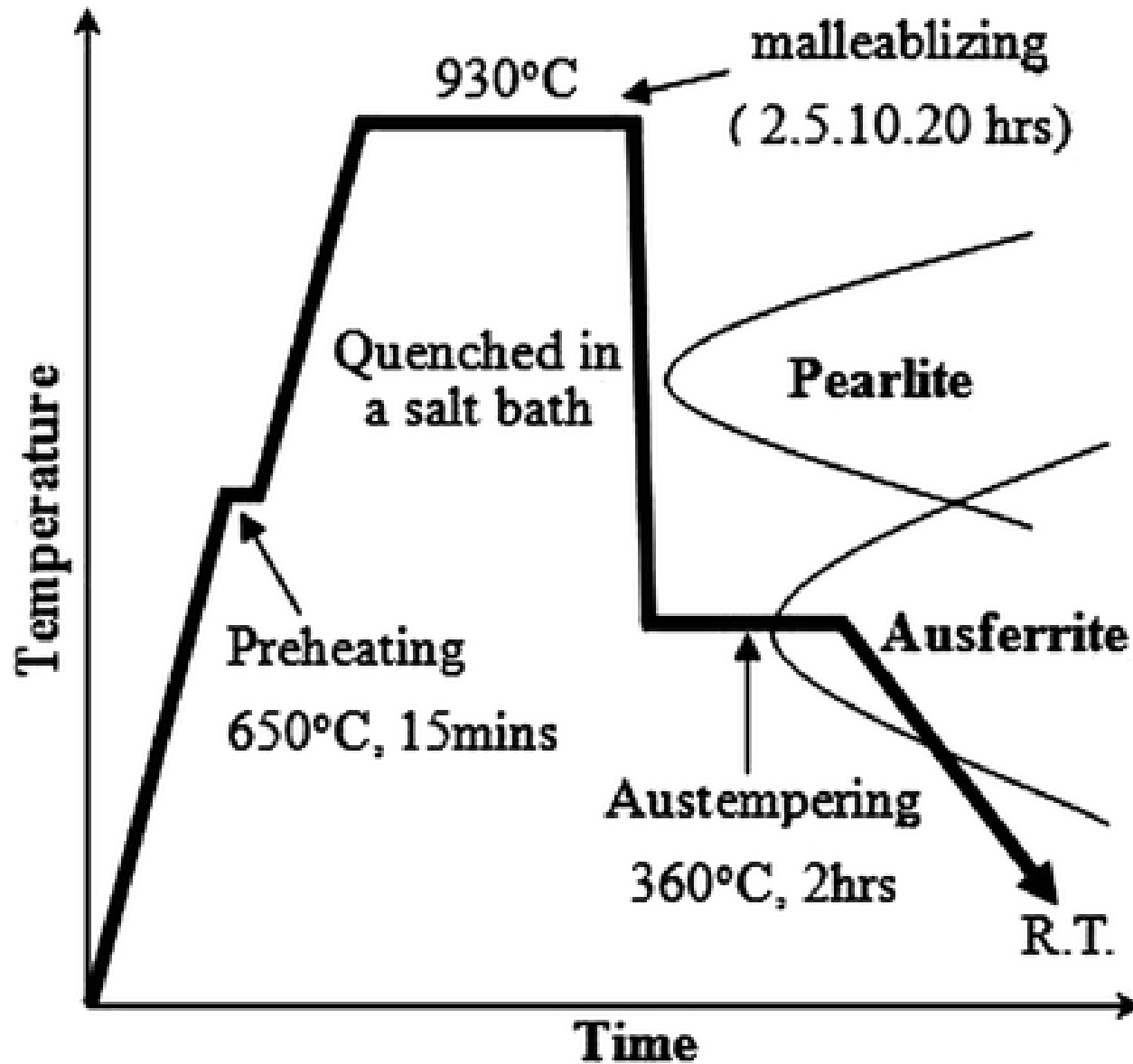


Table 1. Common iron ores^[1]

Mineralogical name	Chemical formula	Chemical composition	Class
Magnetite	Fe_3O_4	72.36% Fe, 27.64% O_2	Oxide
Hematite	Fe_2O_3	69.94% Fe, 30.06% O_2	Oxide
Ilmenite	FeTiO_3	36.80% Fe, 31.63% O_2 , 31.57% Ti	Oxide
Limonite	$\text{HFeO}_2, \text{FeO}(\text{OH})$	62.85% Fe, 27.01% O_2 , 10.14% H_2O	Oxide
Pyrite	FeS_2	46.55% Fe, 53.45.5% S	Sulfide
Siderite	FeCO_3	48.20% Fe, 37.99% CO_2 , 13.81% O_2	Carbonate

Table 2. Typical composition of unalloyed cast irons^[3]

Element	White iron (%)	Malleable iron (%)	Gray iron (%)	Ductile or nodular iron (%)
Carbon	1.8-3.6	2.00-2.60	2.5-4.0	3.0-4.0
Silicon	0.5-1.9	1.10-1.60	1.0-3.0	1.8-2.8
Manganese	0.25-0.80	0.20-1.00	0.25-1.0	0.10-1.00
Sulfur	0.06-0.20	0.04-0.18	0.02-0.25	0.03 max
Phosphorus	0.06-0.18	0.18 max	0.05-1.0	0.10 max

Table 3. Common grades of ductile iron^[3]						
Type (TS-YS -%El)	Tensile strength (ksi)	Yield Strength (ksi)	Elong. (%)	Hardness (BHN)	Heat treatment	Typical microstructure
60-40-18	60	40	18	137-170	Annealed	All ferrite
65-45-12	65	45	12	149-229	-	Ferritic
80-55-06	85	55	6	179-255	-	Ferrite and pearlite
100-70-03	100	70	3	229-302	Normalized	All pearlite
120-90-02	120	90	2	250-350	Quench & Temper	Tempered martensite

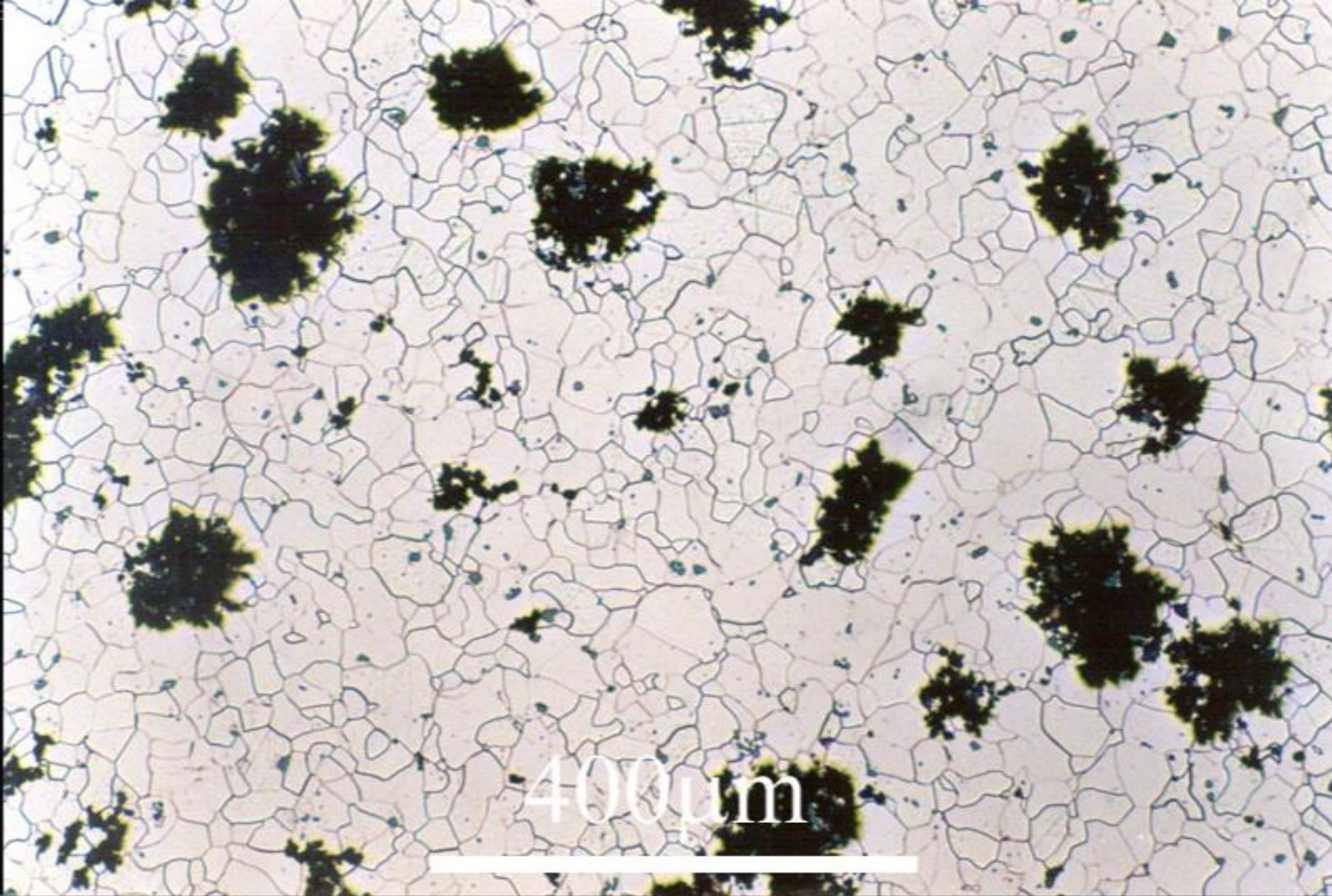
Table 4. Annealing processes for gray and ductile iron castings^(a)

Annealing type	Material	Purpose	Temperature ^(b) °C (°F)	Time	Cooling rate ^(c)
Ferritizing (low-temperature annealing)	Gray iron	Conversion of ferrite to pearlite in unalloyed irons for maximum machinability.	705-760 (1300-1400)	¼ hour per inch of cross-sectional area.	Furnace cool at 38°C/hour (100°F/hour) to 315°C (600°F). Cool in still air from 315°C (600°F) to room temperature.
	Ductile iron	In the absence of carbides to obtain grades 60-45-12 and 60-40-18.	720-730 (1325-1350)	1 hour per inch of cross-sectional area.	Furnace cool at 38°C/hour (100°F/hour) to 345°C (650°F). Air cool.
Full (medium temperature)	Gray iron	Conversion of ferrite to pearlite in unresponsive to low-temperature annealing; elimination of minor amounts of well-dispersed carbides in unalloyed irons.	815-900 (1500-1650)	1 hour per inch of cross-sectional area.	Furnace cool to 315°C (600°F). Cool in still air from 315°C (600°F) to room temperature.
	Ductile iron (lower Si-content iron)	In the absence of carbides to obtain grade 60-40-18.	870-900 (1600-1650)	Only long enough to equalize at control temperature	Furnace cool at 38°C/h (100°F/hour) to 345°C (650°F). Air cool.
Full (Graphitizing, high temperature)	Gray iron	Elimination of massive carbides in mottled or chilled irons and conversion of ferrite to pearlite in unalloyed irons for maximum machinability.	900-955 (1650-1750)	1-3 hours plus 1 hour per inch of cross-sectional area	Furnace cool to 315°C (600°F). Cool in still air from 315°C (600°F) to room temperature
	Ductile iron	In the presence of carbides to obtain grades 60-45-12 and 60-40-18.	900-924 (1650-1700)	2 hours minimum	Furnace cool at 95°C/hour (200°F/hour) to 705°C (1300°F). Hold 2 hours. Furnace cool at 38°C/hour (100°F/hour) to 345°C (650°F). Air cool.
Two-stage graphitization and ferritizing	Ductile iron	In the presence of carbides to obtain grades 60-45-12 and 60-40-18 where rapid cooling is practical.	900-924 (1650-1700)	1 hour per inch of cross-sectional area	Fast cool to 675°C (1250°F). Reheat to 730°C (1350°F) Hold 2 hours. Furnace cool at 38°C/hour (100°F/hour) to 345°C (650°F). Air cool.
Normalize Anneal	Gray iron	Elimination of massive carbides with the retention of pearlite for strength and hardness.	870-955 (1600-1750)	1-3 hours plus 1 hour per inch of cross-sectional area ^(b)	Air cool to below 480°C (900°F). May require subsequent stress relief.
Normalizing and tempering stress relief	Ductile iron		900-924 (1650-1700)	2 hours minimum	Air quench with fans. Temper at 540-675°C (1000-1250°F). Furnace cool at 38°C/hour (100°F/hour) to 345°C (650°F). Air cool.

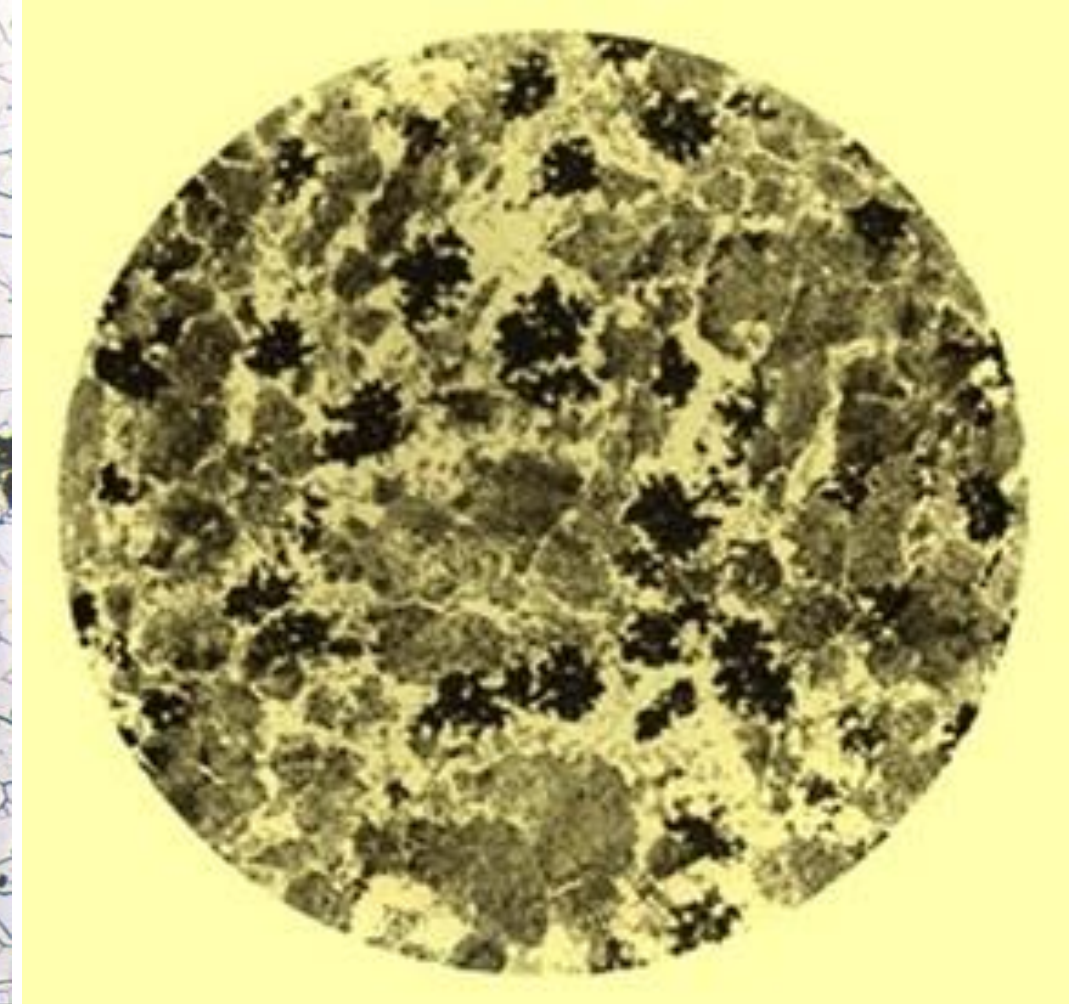
Notes: ^(a) Preferred temperature for castings is dependent on silicon, manganese and the alloy content.

^(b) Time for graphitization will vary from 30-60 minutes in unalloyed irons to 2-3 hours in irons containing carbide stabilizers.

^(c) Slow cooling from 540-315°C (1000-600°F) is necessary to minimize residual stress.



c. Ferritic matrix



d. Perlitic - Ferritic matrix

1.2 Graphitizing Elements

- In fact, for achieving the formation of graphite in the case of eutectic liquids and industrial cooling rates, even if they are slow, the presence of graphitizing elements, such as **Si, P, Al, Ni or Cu** (listed in descending order of efficiency) is required. The presence of these elements in the liquid is effective due to both the dilution and the affinity (activity) effects.
- Graphitizing elements dissolve the pre-clusters of Fe and C necessities for the formation of cementite clusters. Consequently, the cementite kinetics is retarded, and the appearance of graphite is made possible. On the other hand, some elements—such as Si, P, Al—with an affinity for the iron (to form silicides, phosphides, aluminides) add, to the dilution simple effect above mentioned, a tendency to form graphite instead of cementite.

1.3 Inoculant Elements

- **Ferrosilicon** and some compounds that are called inoculants—such as **calcium silicides, zirconium alloys, strontium alloys, etc.—accelerate the graphite formation.** That is because they facilitate the heterogeneous nucleation of the graphite, **by epitaxy or crystallographic similarity.**
- **The inoculation increases the nucleation rate and the refining of the graphite particles;** and it gives origin, also, to the formation of a higher number of eutectic cells.
- Some elements, as magnesium or boron, are in the origin of a spheroidal graphite morphology, instead of the typical laminar morphology. The inoculants efficiency disappears with the time, so, after the inoculation, it is advisable to cast irons as soon as possible

1.4 Carburigenous Elements

- The elements with the aptitude **to form more stable carbides than the cementite, or to stabilize the cementite as a complex carbide—such as titanium, zirconium, niobium, vanadium, tungsten, molybdenum, chromium, manganese—are called anti-graphitizing elements.**
- Obviously, the presence of these elements in the liquid is unfavorable for the graphite nucleation (carbides are preferentially formed); and, therefore, they are harmful for the formation of the eutectic of graphite + austenite. For example, **high-chromium alloyed cast irons**, which are characterized by their abrasion, corrosion and high-temperature resistances, always solidify following the Fe/C metastable diagram as will be studied in Chaps. 8 and 9

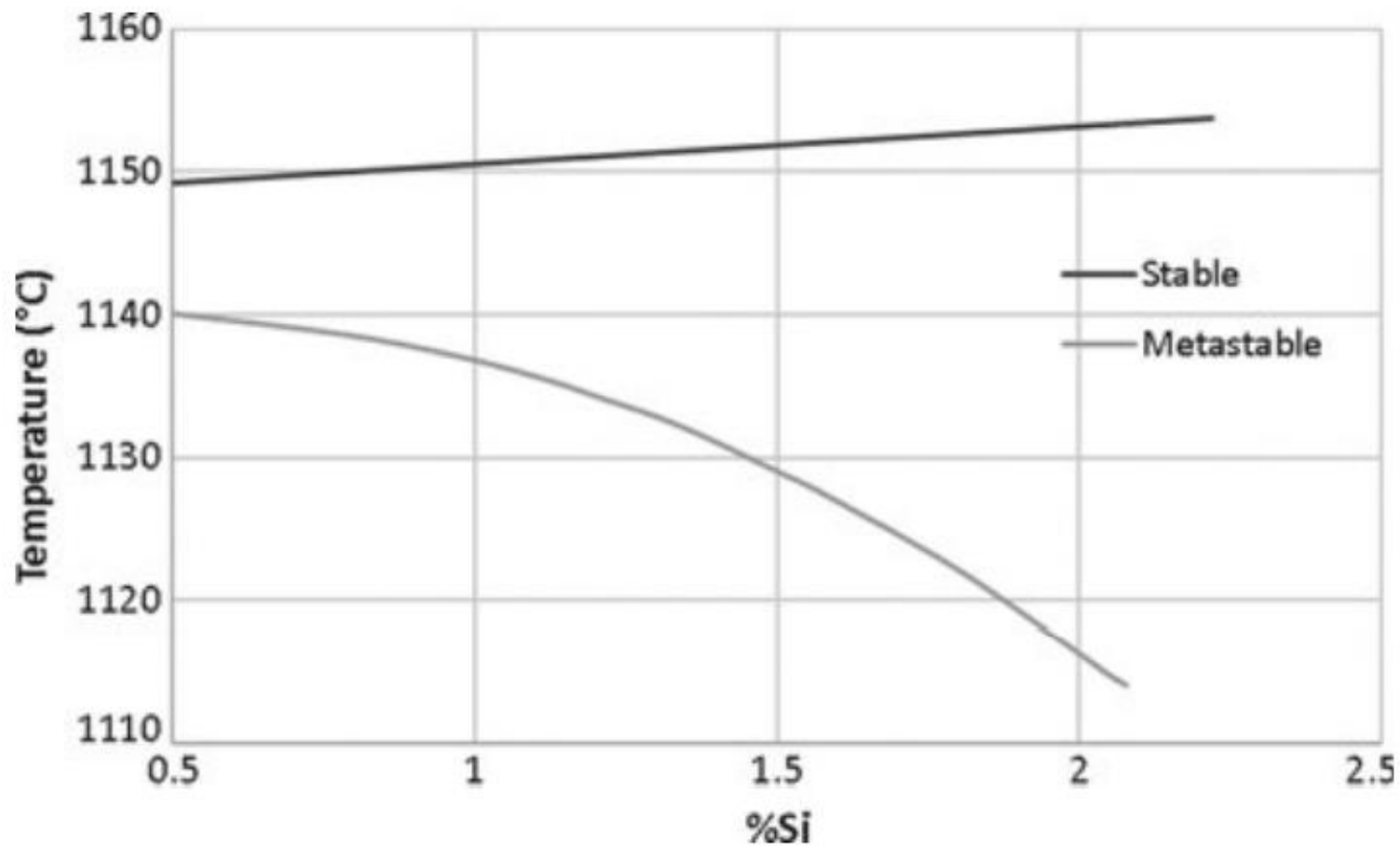


Fig. 1.6 Beginning temperatures of both stable and metastable eutectics as a function of the silicon amount (wt%)

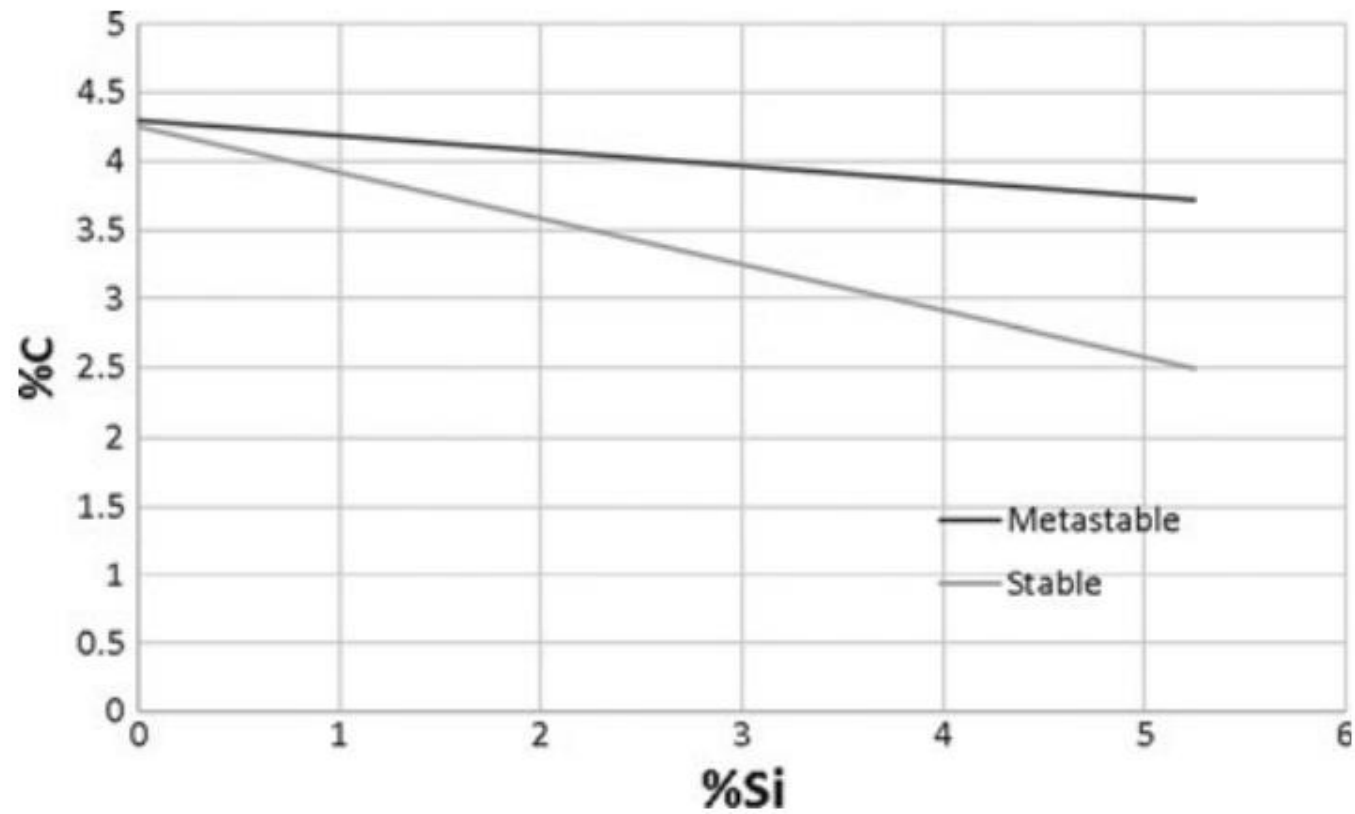


Fig. 1.7 Carbon contents both in the stable and metastable eutectics (wt%) as a function of the silicon

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