Heat Treatment Technology

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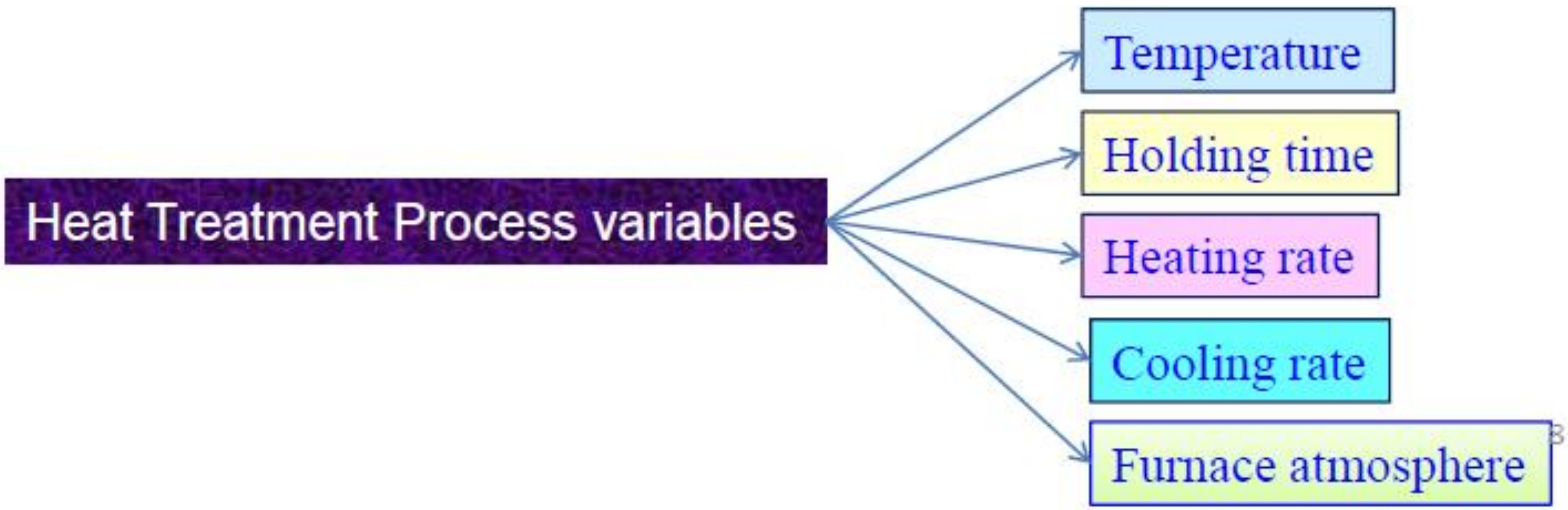
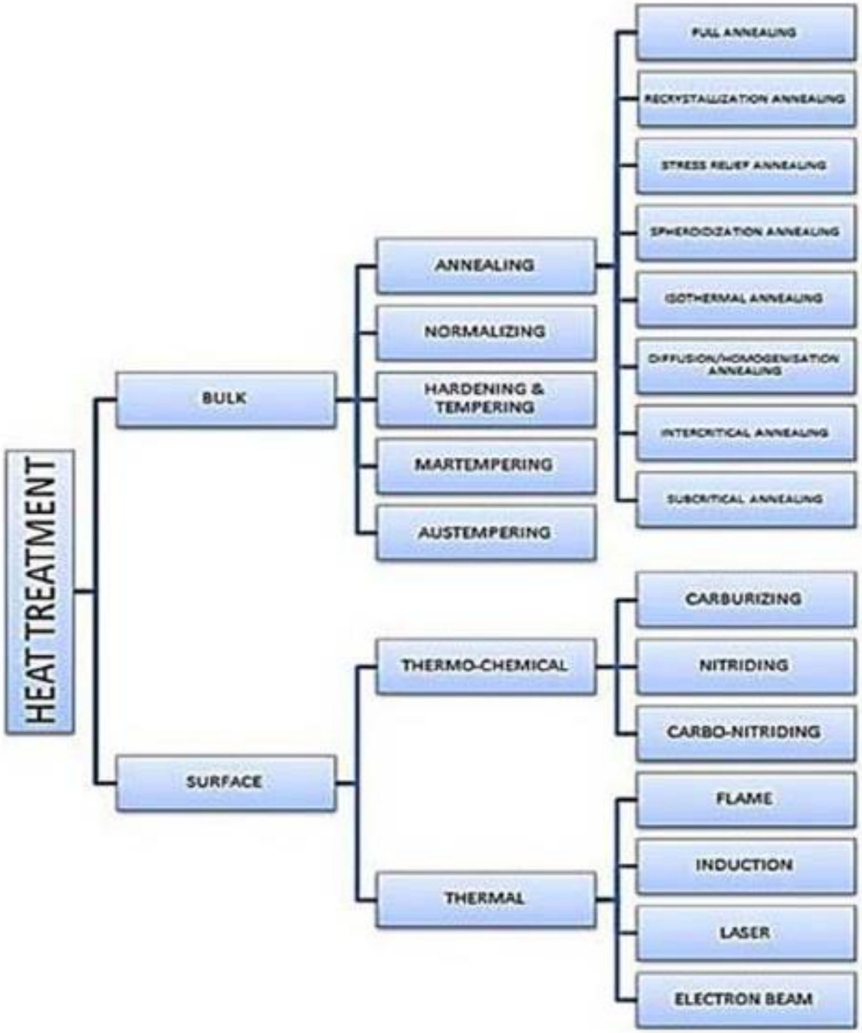
Introduction

Objectives of HT

- **To increase strength, hardness and wear resistance (*bulk hardening, surface hardening*)**
- **To increase ductility and softness (*Tempering, Recrystallization Annealing*)**
- **To increase toughness (*Tempering, Recrystallization annealing*)**
- **To obtain fine grain size (*Recrystallization annealing, Full annealing, Normalizing*)**
- **To remove internal stresses induced by differential deformation by cold working, nonuniform cooling from high temperature during casting and welding (*Stress relief annealing*)**
- **To improve machinability (*Full annealing and Normalizing*)**
- **To improve cutting properties of tool steels (*Hardening and Tempering*)**
- **To improve surface properties (*surface hardening, high temperature resistance-resistance precipitation hardening, surface treatment*)**
- **To improve electrical properties (*Recrystallization, Tempering, Age hardening*)**
- **To improve magnetic properties (*Hardening, Phase transformation*)**


Heat Treatment Process variables
Temperature
Holding time
Heating rate
Cooling rate
Furnace atmosphere



- **Cool in the furnace (normally 50°C/hr) i.e., the furnace is switched off**.
- **Full annealing** (Above A3)
- **Recrystallization annealing** (Tr = (0.3 – 0.5) $T_{m.P.}$ in K) about 650°C to 680°C for CS,
- **Stress Relief annealing**
  1. Slow heating in a furnace at a rate of 100-150°C/h up to 650°C.
  2. Soaking at this temperature for a definite time based on maximum thickness at the rate of 3-4 minutes/mm to attain uniformity of temperature.
  3. Slow cooling of 50-100°C/h to at least 300°C and then cooled in air to room temperature.
- **Spheroidization** (close to A1 temperature, requiring more than 200 hours.)
- **Isothermal annealing**
- **Solution/ Diffusion / Homogenization** (at 1150°C to 1200°C for 10-20 hours followed by slow cooling)
- **Inter-critical annealing** (between Ac1 and Ac3)
- **Sub-critical annealing** (below Ac1)

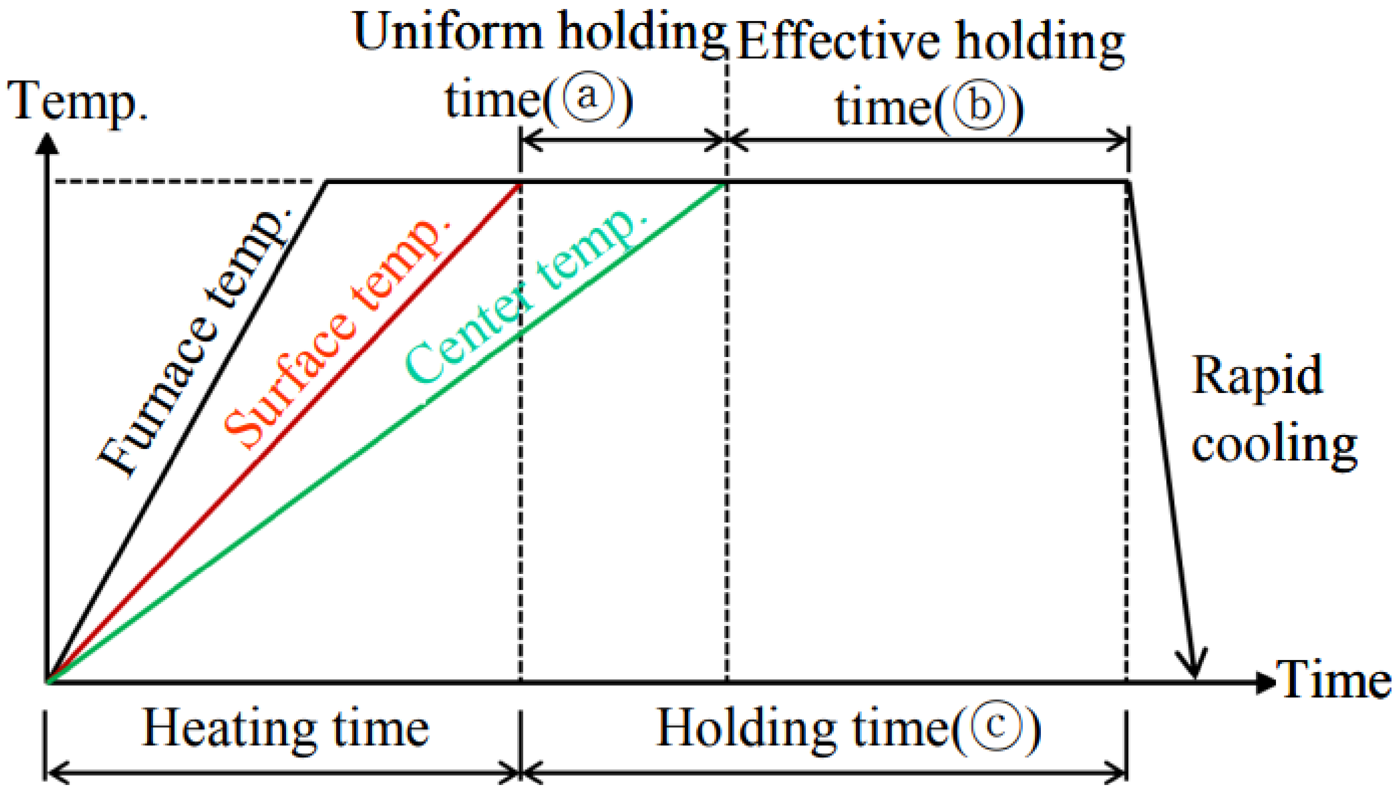
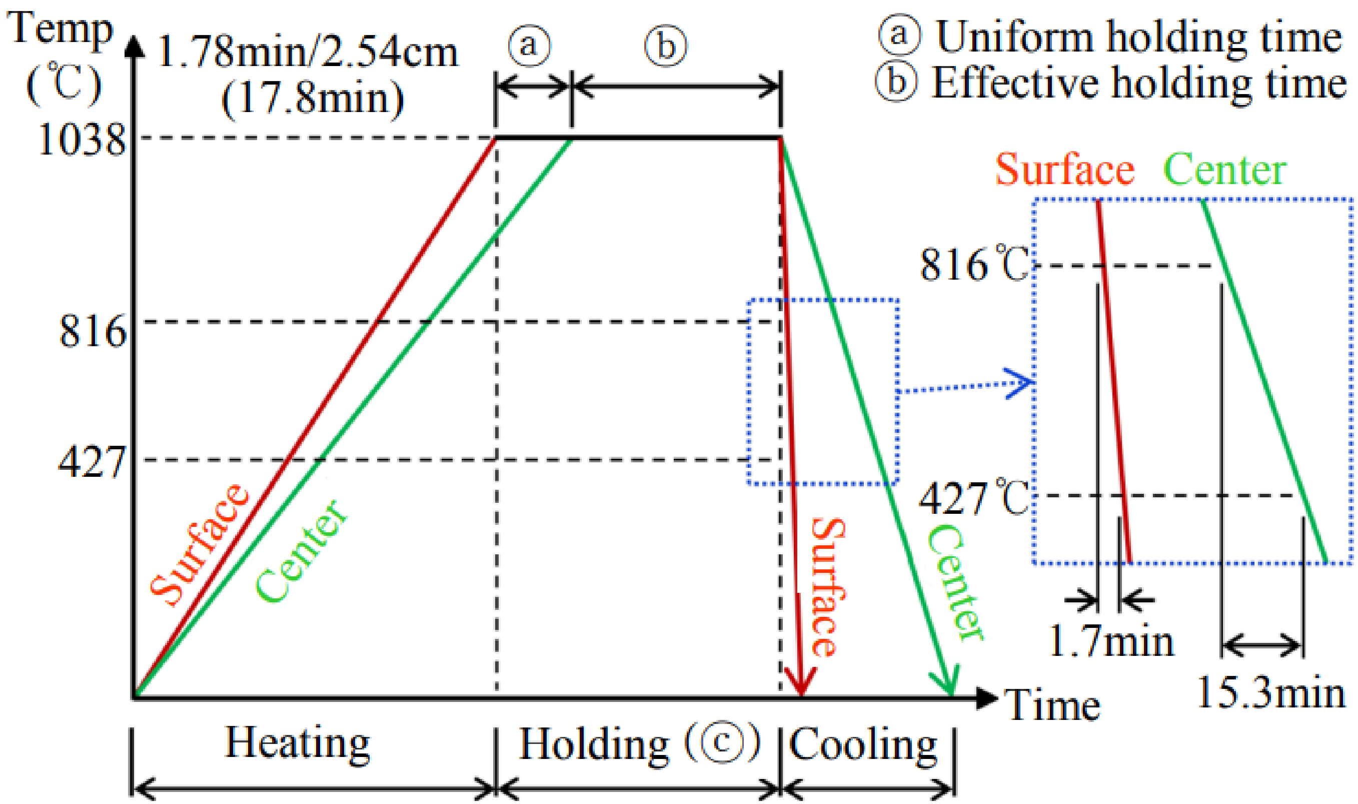


Fig. 1 Schematic diagram of solution heat treatment cycle



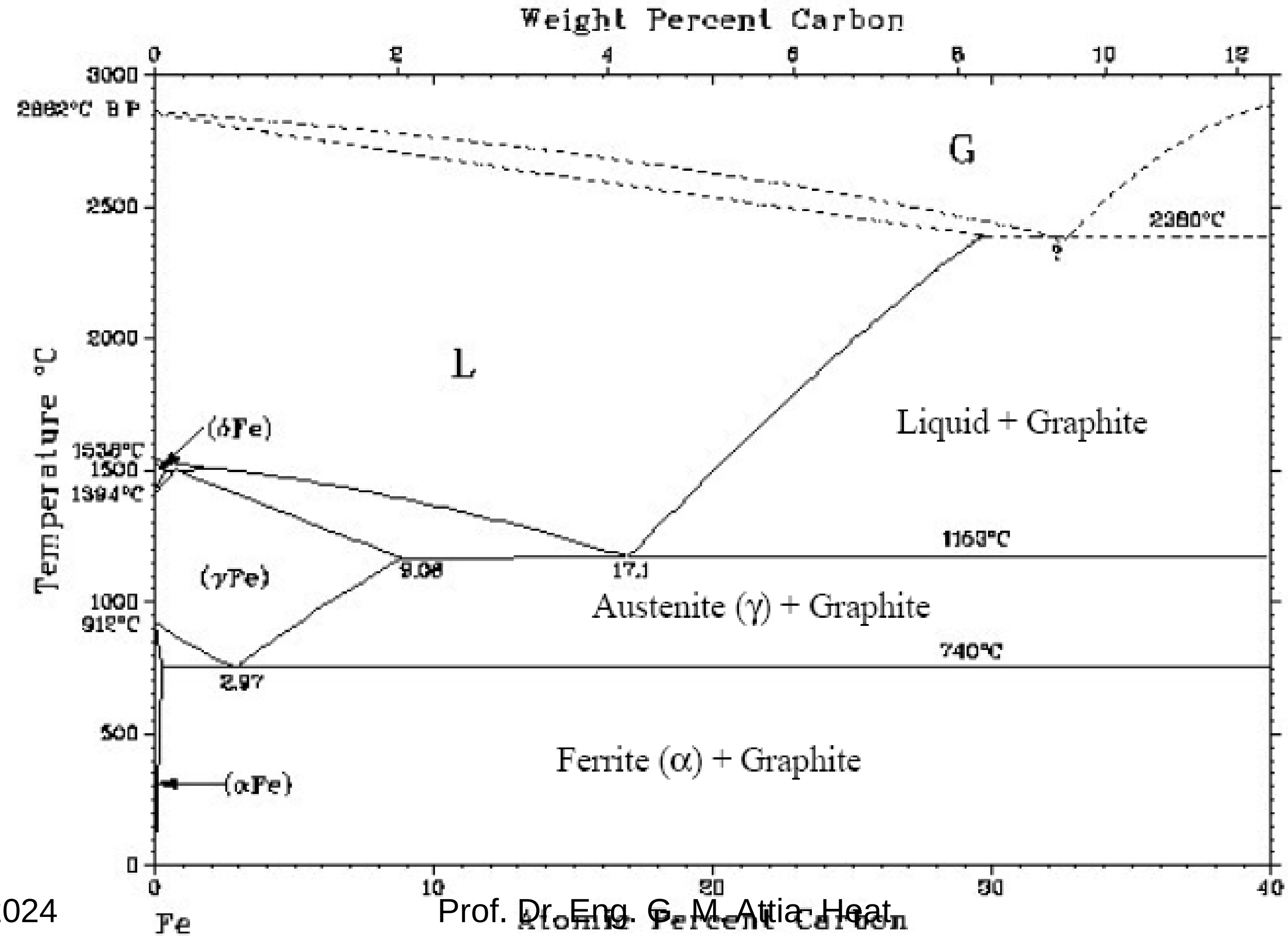
Schematic diagram of the 25.4cm-thick specimen solution heat-treated at 1,038℃ for 5h measured by thermocouples

Introduction to Cast Iron Metallurgy

Introduction to Gray Cast Iron Metallurgy

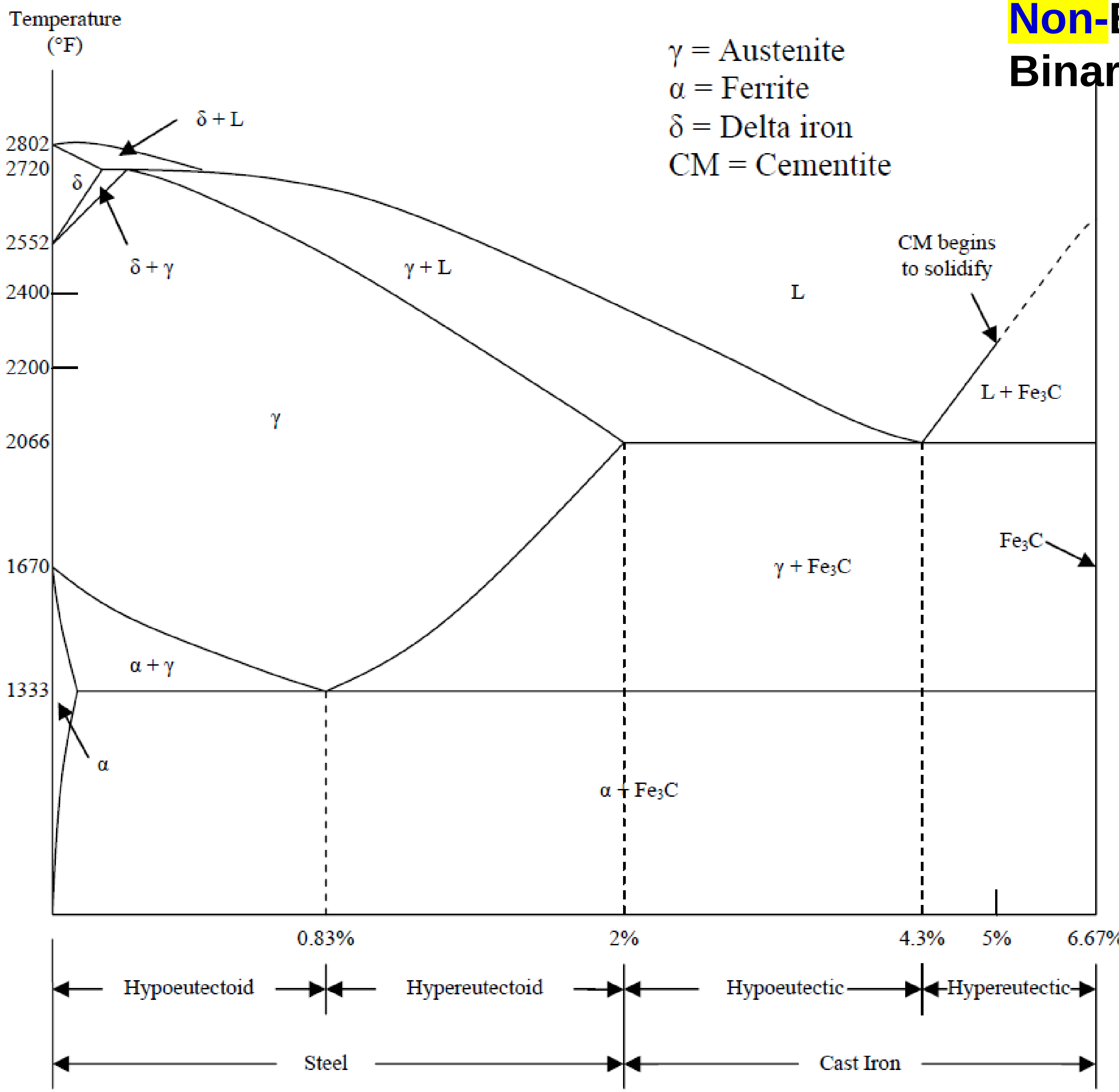
- The **properties** of cast iron components are **controlled by** the **microstructure** of the material, which consequentially is determined by the **chemistry and processing of the cast iron (Heat and liquid Treatment).**

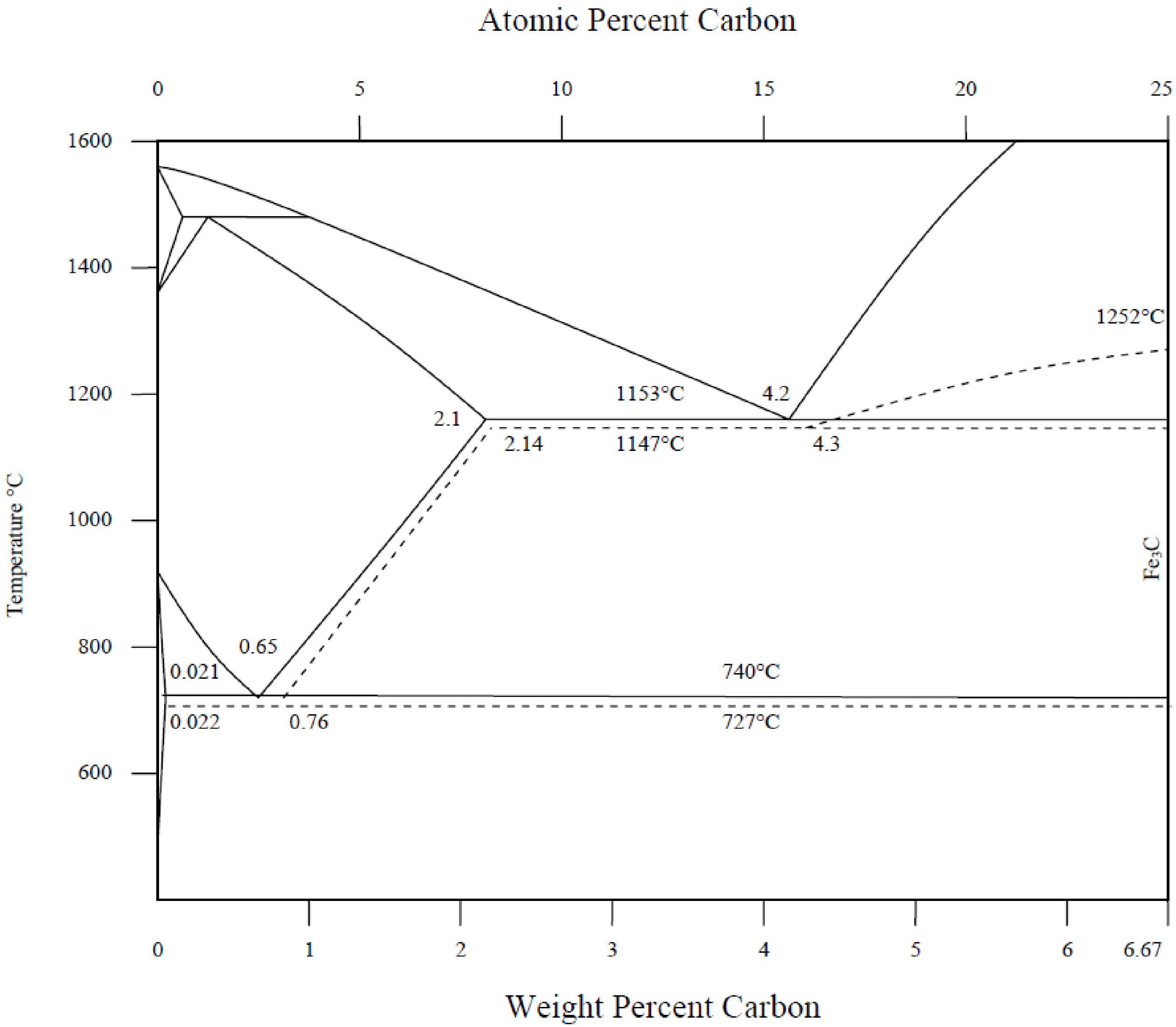
Equilibrium Iron-Carbon Binary Phase Diagram



3675 ºC

Non-Equilibrium Iron-Carbon Binary Phase Diagram





Metastable Iron-iron carbide (dotted lines) **and Stable** - true equilibrium phase diagram (bold lines)

Equilibrium Solid Phases in the Binary Iron-Carbon System

- Ferrite (α-Fe)
- Austenite (γ-Fe)
- Delta Iron (δ-Fe)
- Graphite (C)

<u>Microstructure Constituents</u>

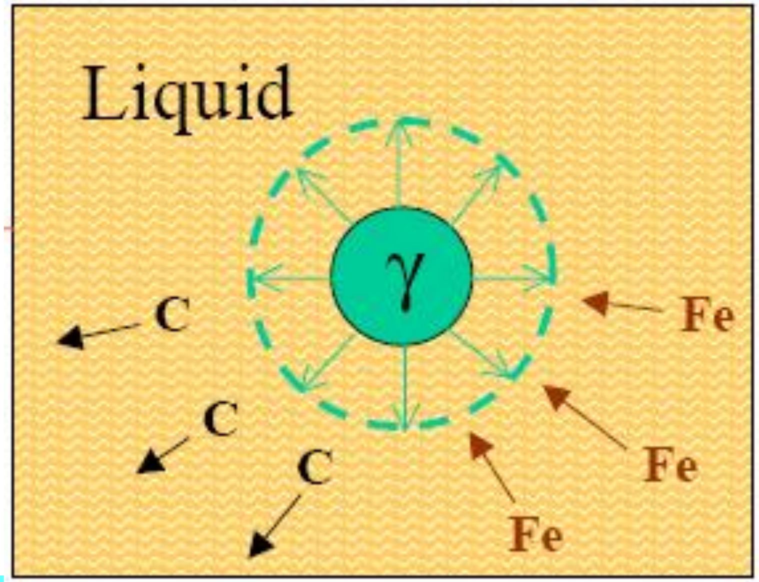
Pearlite, Ledeburite (transformed Ledeburite)

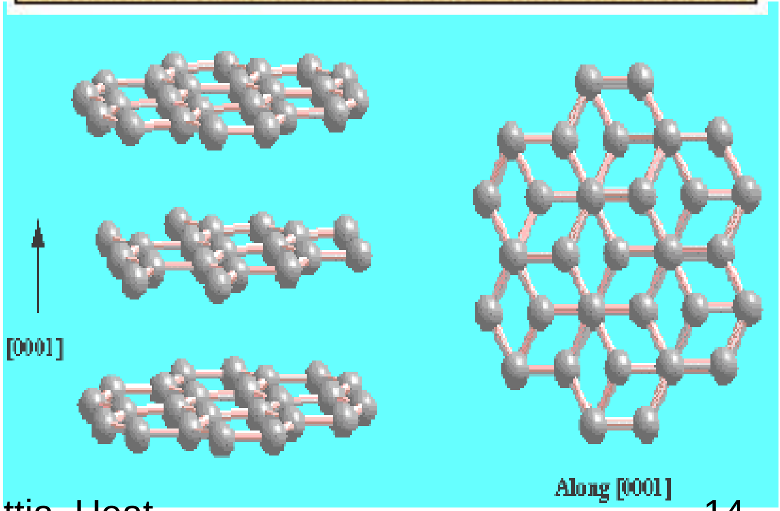
<u>Meta stable phases</u>

Cementite, Martensite, Bainite (acicular ferrite),

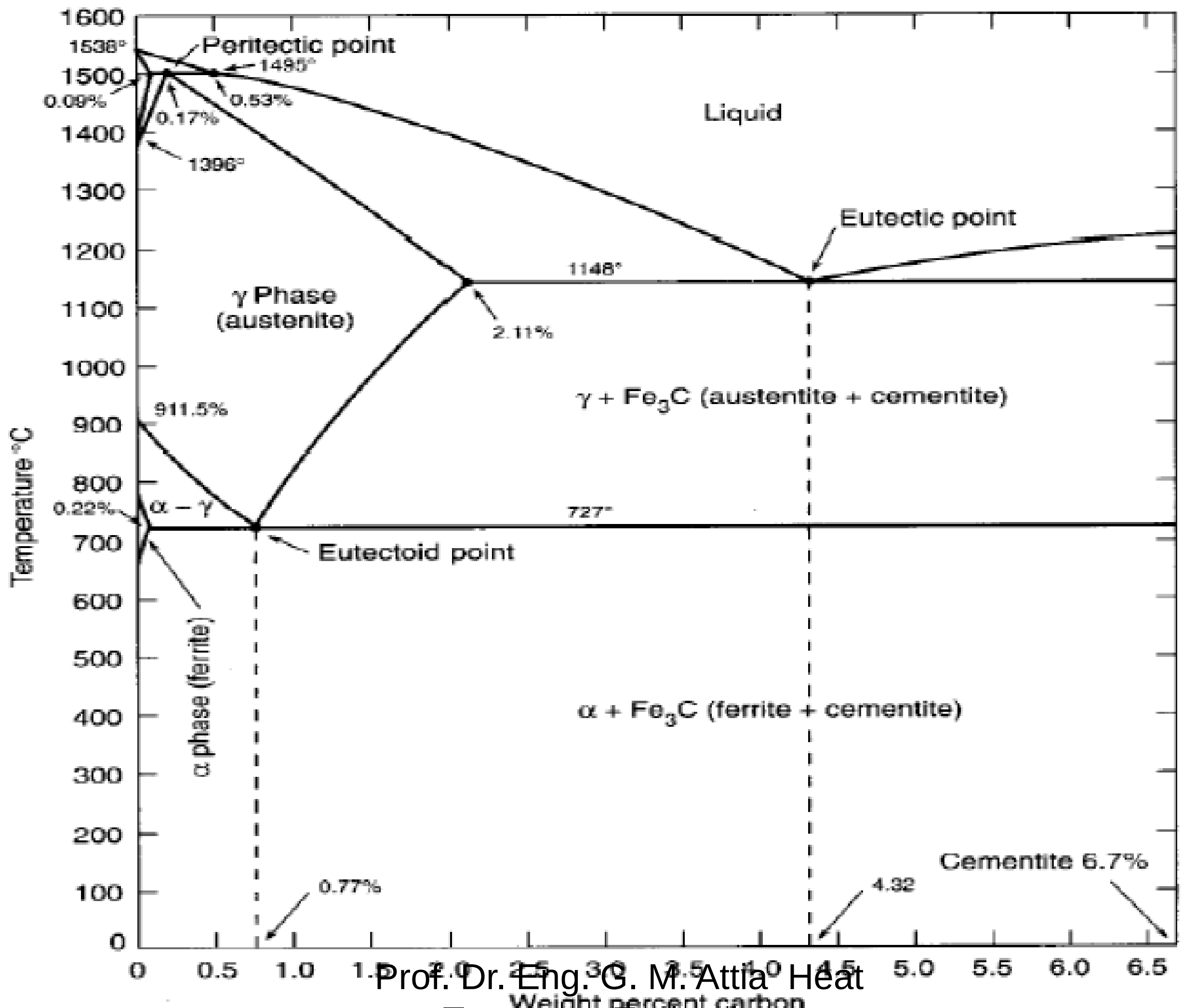
Graphite Carbon Phase

- Layered **hexagonal** structure with covalent bonding of atoms in each layer
- **Density:** 2.25 grams/cm^3 at 20°C
- Layers easily slide against each other and make graphite a solid lubricant
- **Soft and low strength**
- **Primary and secondary precipitates**





Meta-Stable Iron-Iron Carbide Binary Phase Diagram



Meta-Stable Iron-Carbon System

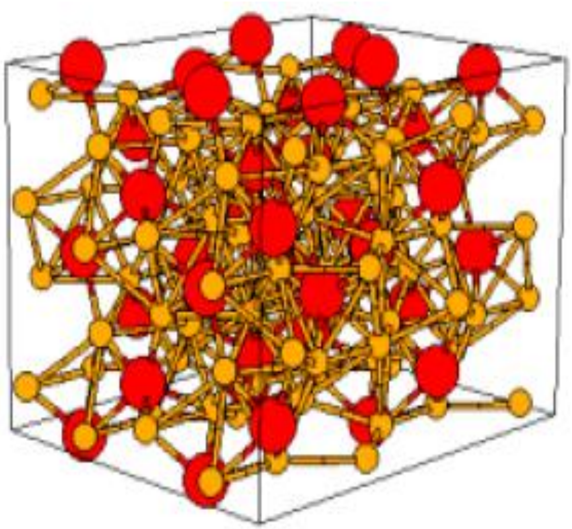
The formation of graphite in the equilibrium iron-carbon system is dependent upon the diffusion of carbon through the iron matrix to form the graphite precipitates.

If the cooling rate is fast, then the carbon is not able to segregate, and iron carbide (Fe_3C) forms in place of graphite.

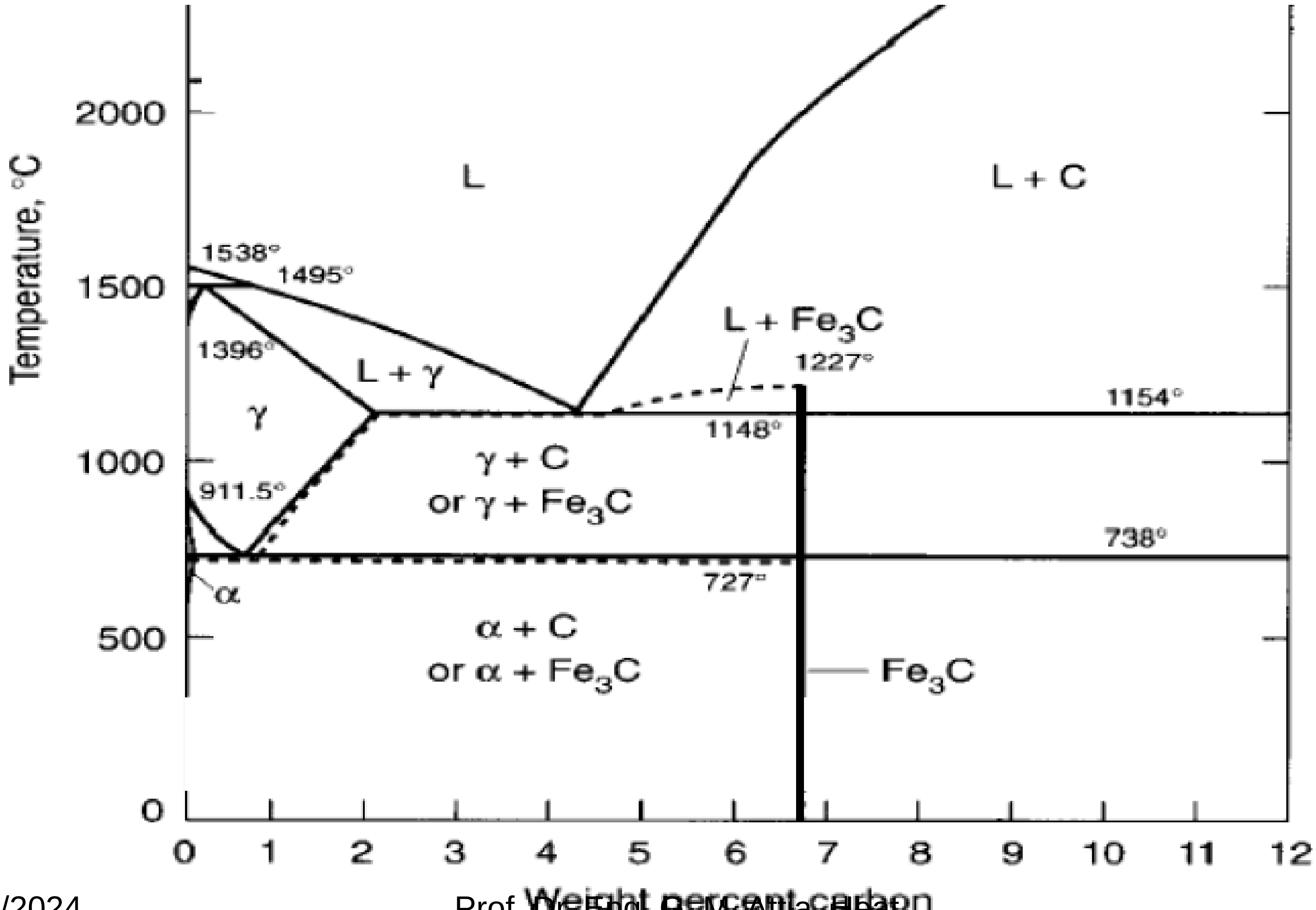
This meta-stable system is commonly called the iron-iron carbide system.

Iron Carbide Phase

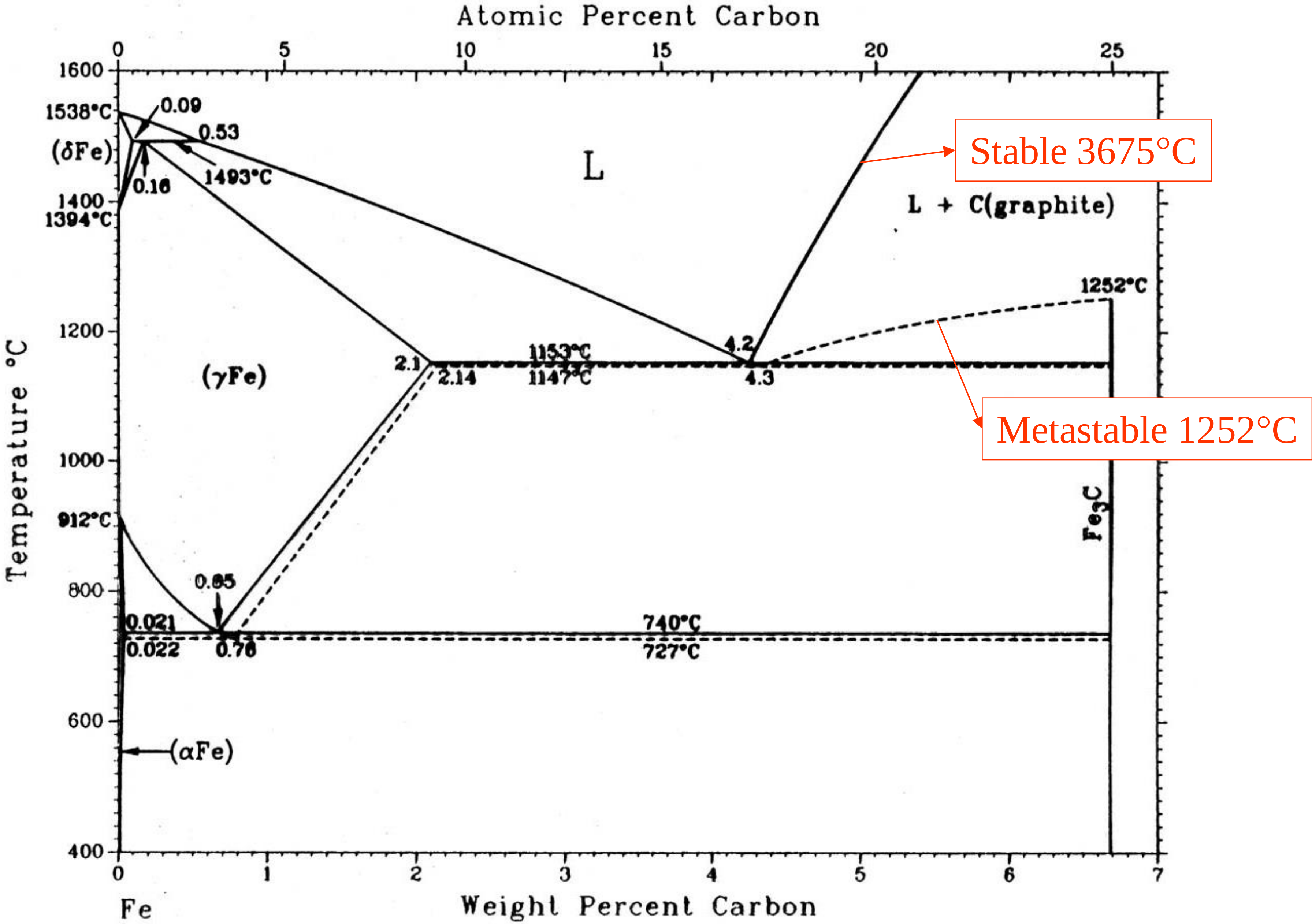
- **Fe_3C** is the chemical composition, and it has **orthorhombic crystal structure**.
- Iron carbide breaks down to iron and graphite with sufficient time and temperature.
- For practical purposes it is considered stable below 450°C.
- **Density: 7.66** grams/cm^3 at 20°C
- **Very hard and brittle** phase
- Commonly called “cementite”
- **Melting point 1227°C**



Combination of Equilibrium and Meta-Stable Phase Diagrams



Fe-C Phase Diagram

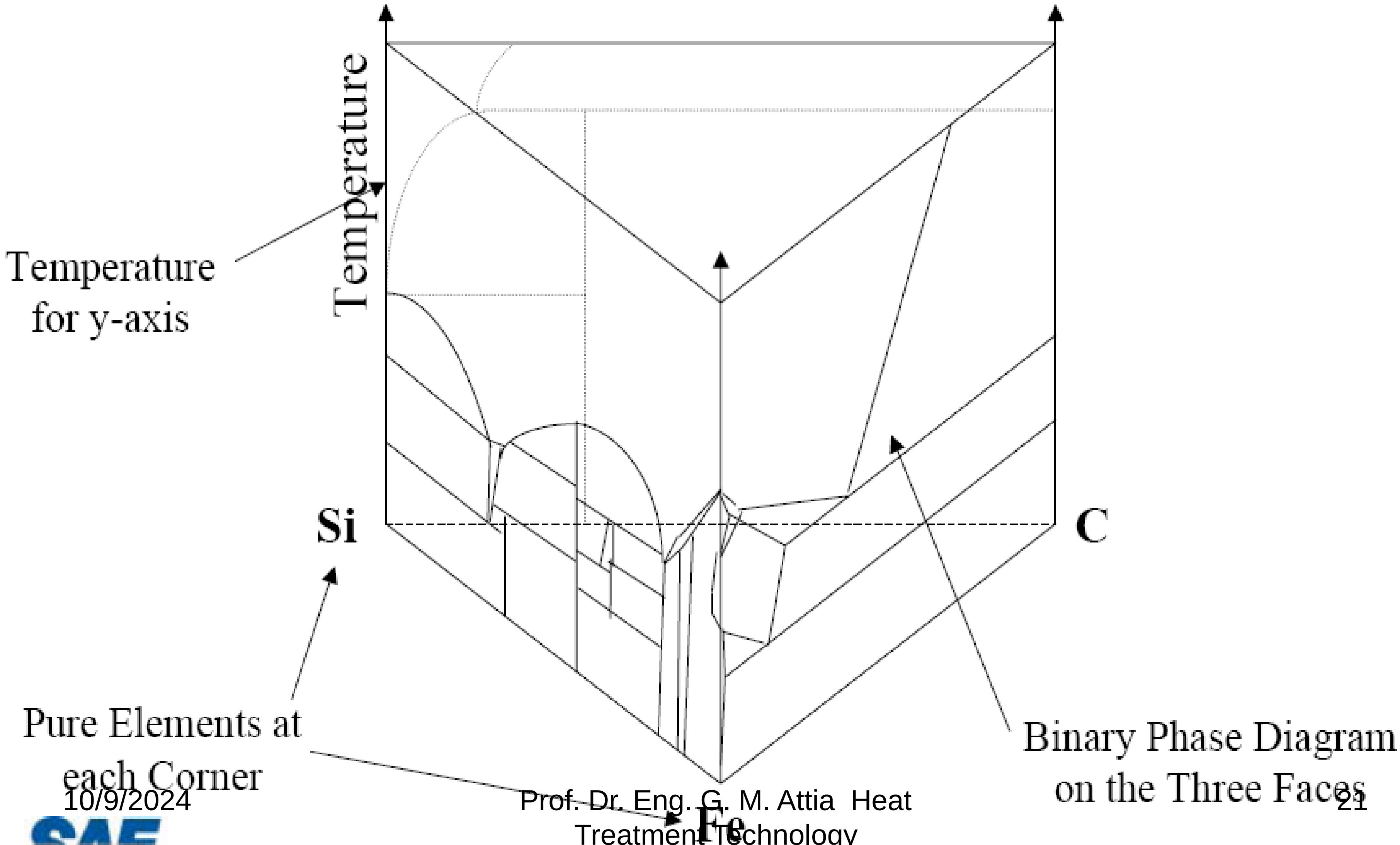


Cast iron is not a binary alloy

Fe-C-Si is a ternary alloy or Fe-C-Si-Mn a quaternary alloy

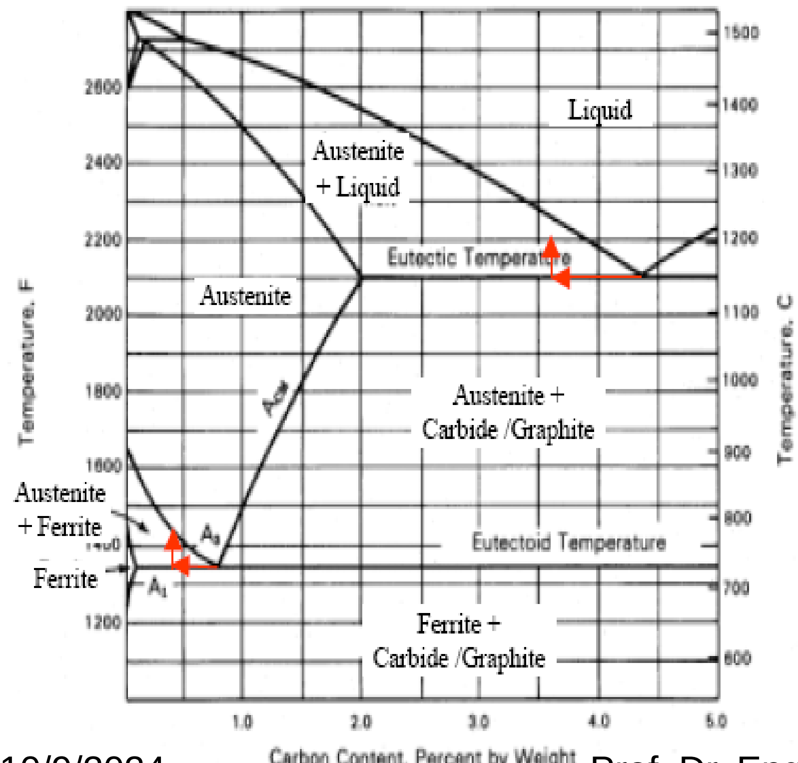
1. **The Addition of Silicon to the Iron-Carbon System**
   - **Silicon** is added to cast irons in the range of **1% to 4%** in order to increase the amount of under-cooling required for the formation of cementite and **promote the formation of graphite during solidification.**
   - The range of silicon added is sufficient that, the iron-carbon binary phase diagram is insufficient to predict the phases and microstructures that form.
   - The iron-carbon-silicon ternary phase diagram and/or sections of this diagram are needed to properly predict the phases and microstructures that form.
2. **The Addition of Mn to the Iron-Carbon System**
   - **Manganese** is a carbide-forming element, so it is added (**1 to 1.25%**) to **inhibit graphitization** .

Iron-Carbon-Silicon Ternary Phase Diagram

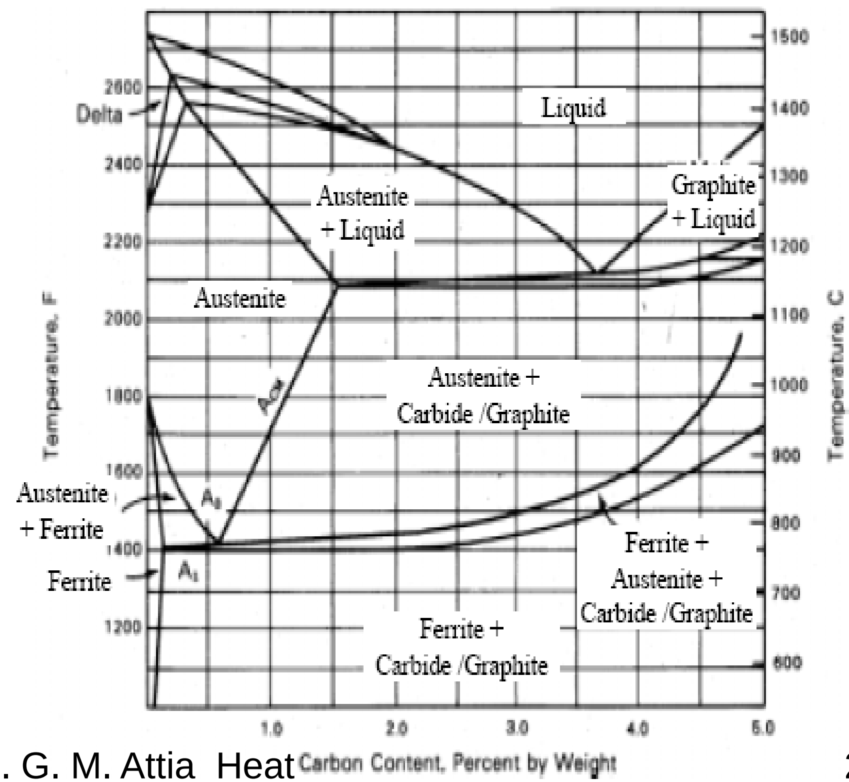


Effects of Silicon on the Eutectic and Eutectoid Transformations

Iron-Carbon
Phase Diagram

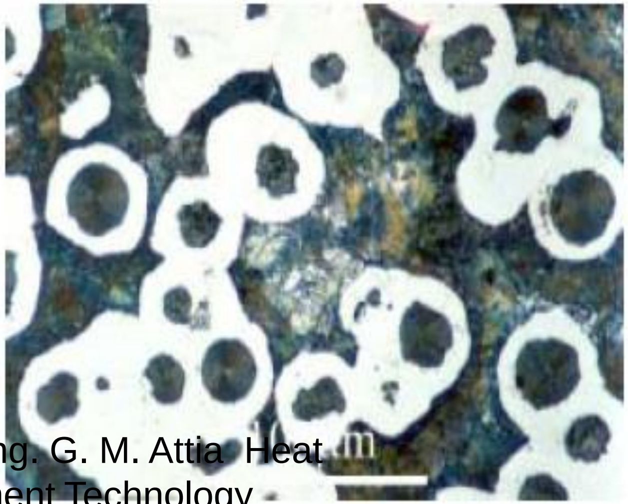


Iron-Carbon-Silicon(2%)
Phase Diagram



Microstructural Effects of Silicon Additions in Cast Irons

- Silicon strongly reduces the potential for eutectic carbides during solidification and promotes the formation of **primary graphite**.
- Silicon promotes the precipitation of **secondary graphite** on the primary graphite during the eutectoid transformation, which results in large areas of ferrite (commonly called “free ferrite”) around the graphite particles.



Classifications of Cast Irons

- Classifications are determined **by the eutectic** graphite/carbide forms present in the iron microstructure.
- Classifications are controlled **by alloying, solidification rates and heat treatment.**
- **Classifications of cast irons**

– White Irons

– Malleable Irons

– Gray Irons

– Ductile Irons

– Compacted Graphite Irons

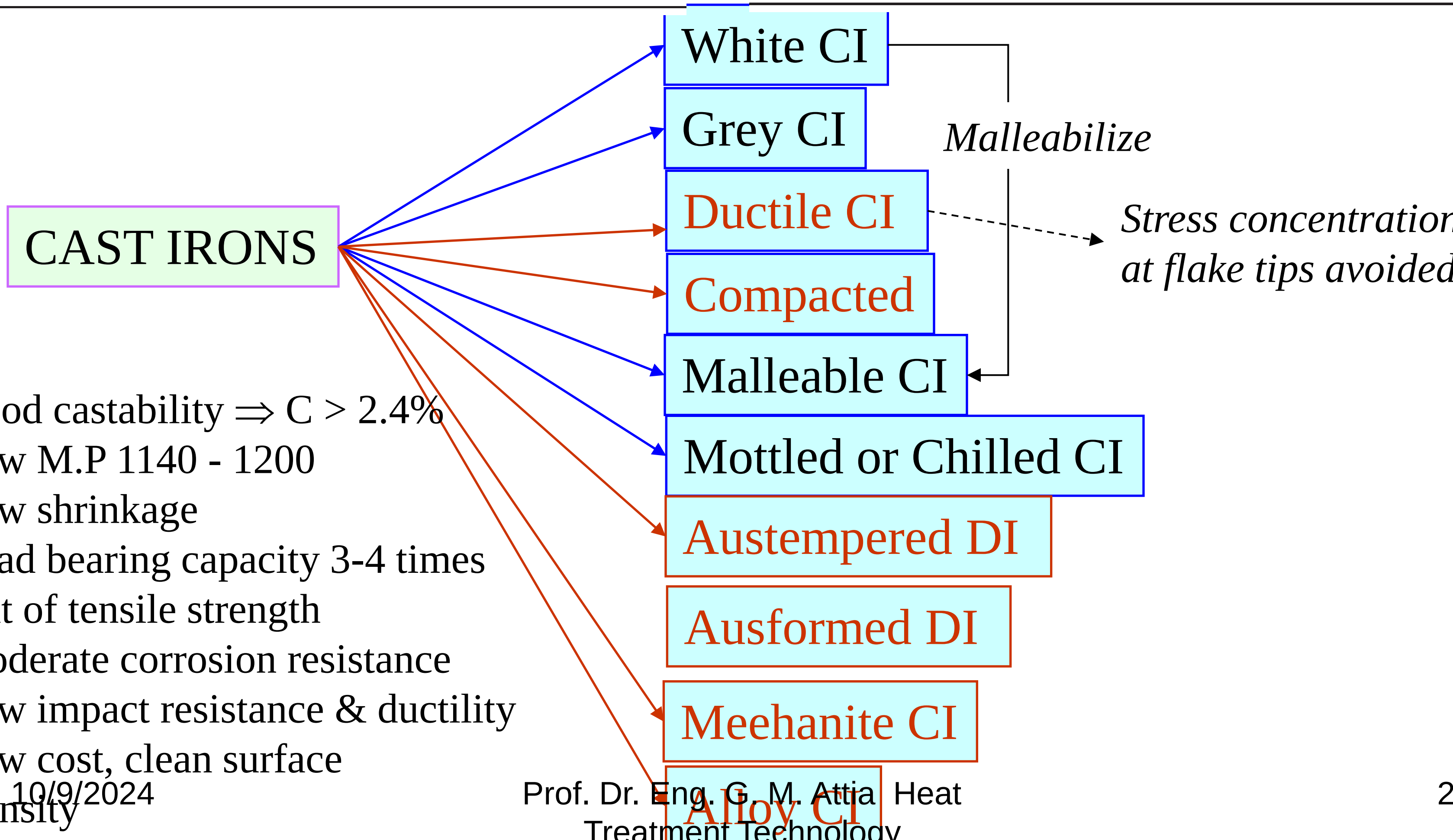
Graphitic Cast Irons

Common unalloyed gray cast iron

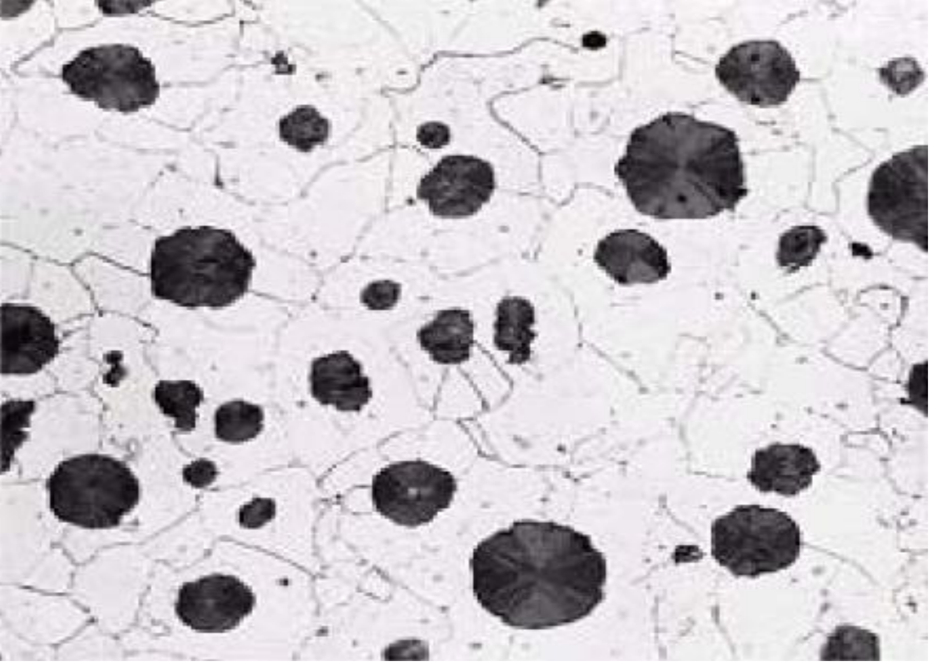
Element	Content, %
Carbon	2.5–4.0
Silicon	1.0–3.0
Manganese	0.2–1.0
Phosphorus	0.002–1.0
Sulfur	0.02–0.25

composition range of unalloyed white iron

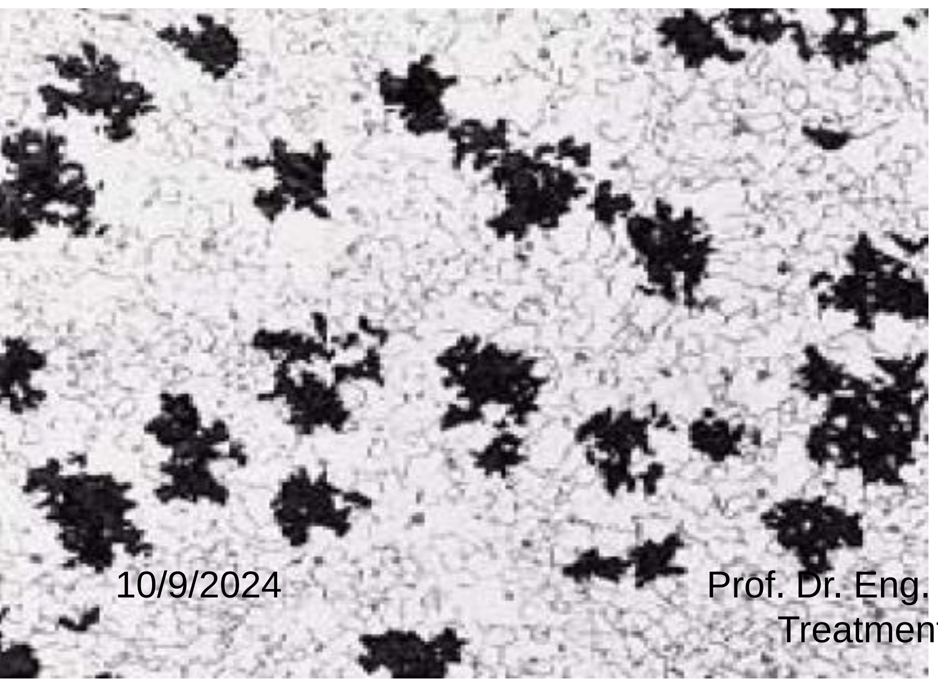
Element	Content, %
Carbon	1.8–3.6
Silicon	0.5–1.9
Manganese	0.25–0.8
Phosphorus	0.06–0.2
Sulfur	0.06–0.2

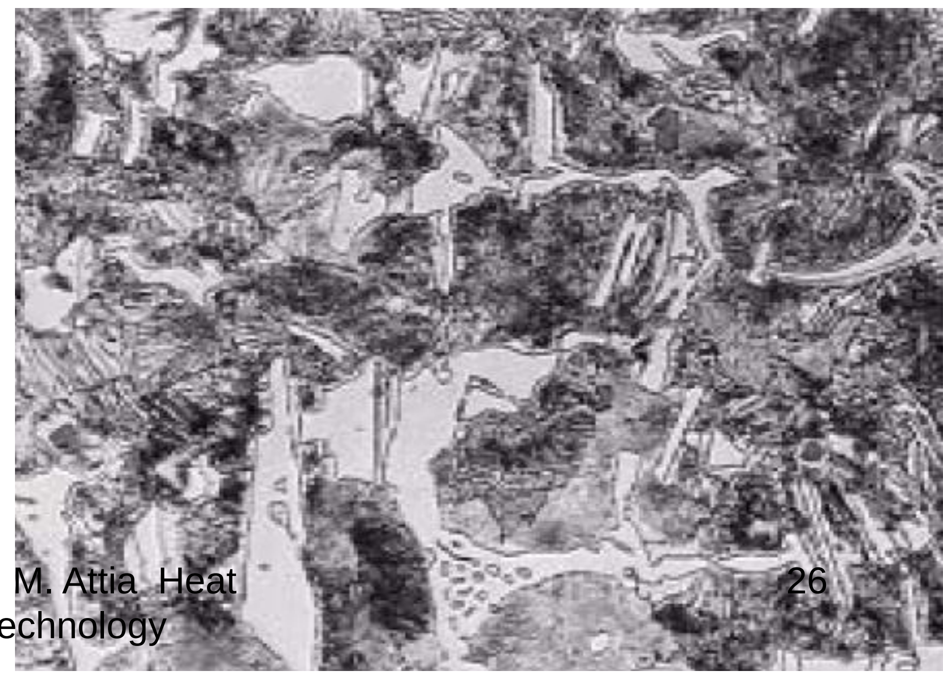


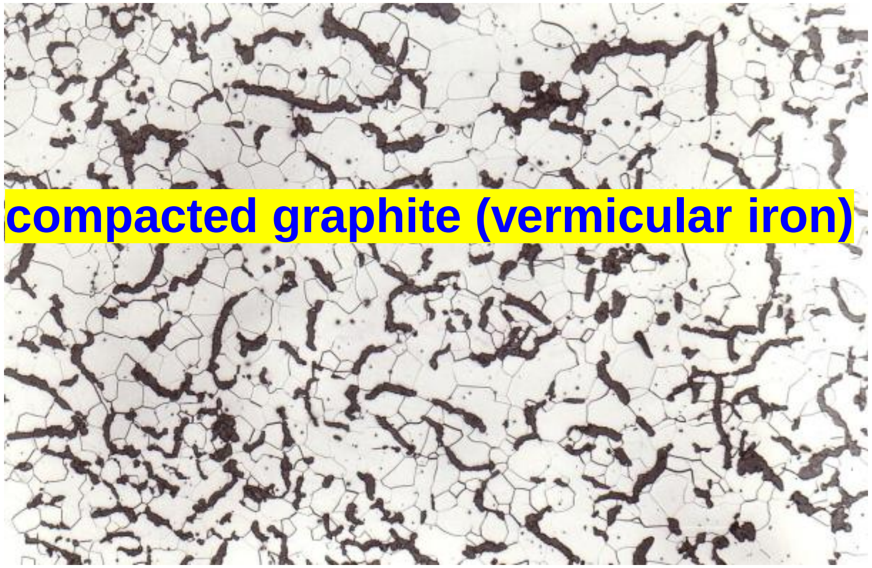
Good castability ⇒ C > 2.4%
Low M.P 1140 - 1200
Low shrinkage
Load bearing capacity 3-4 times that of tensile strength
Moderate corrosion resistance
Low impact resistance & ductility
Low cost, clean surface
Density

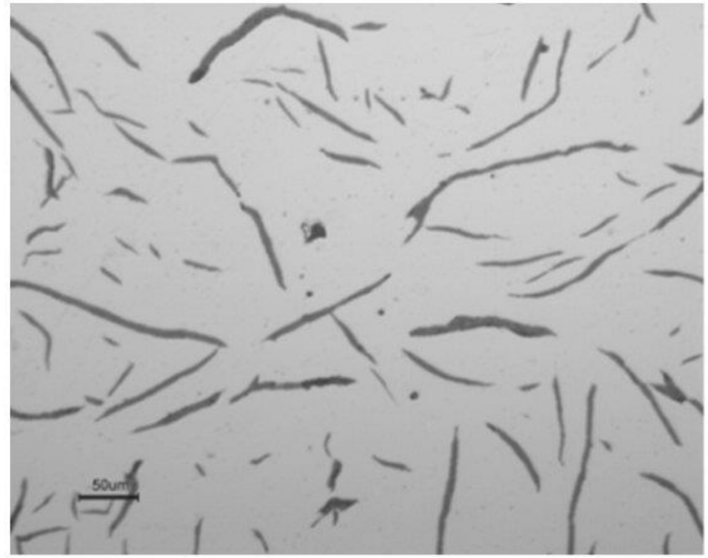


Ductile iron ↑ Malleable iron↓ Gray iron ↑ white iron, ↓

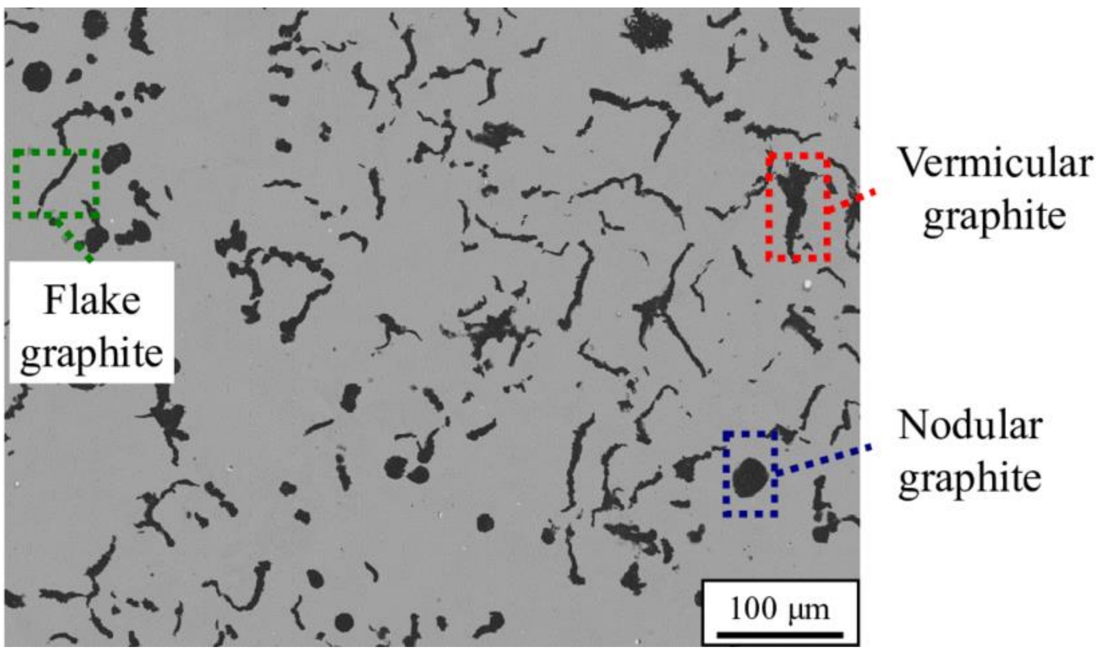








Graphite Flake



As shown in Figure, the graphite in compacted graphite iron (sometimes referred to as vermicular iron) appears as individual ‘worm-shaped’ or vermicular particles. Although the particles are elongated and randomly oriented as in grey iron, the compacted graphite particles are shorter and thicker, and have rounded edges.

Factors affecting the structure and properties of cast iron

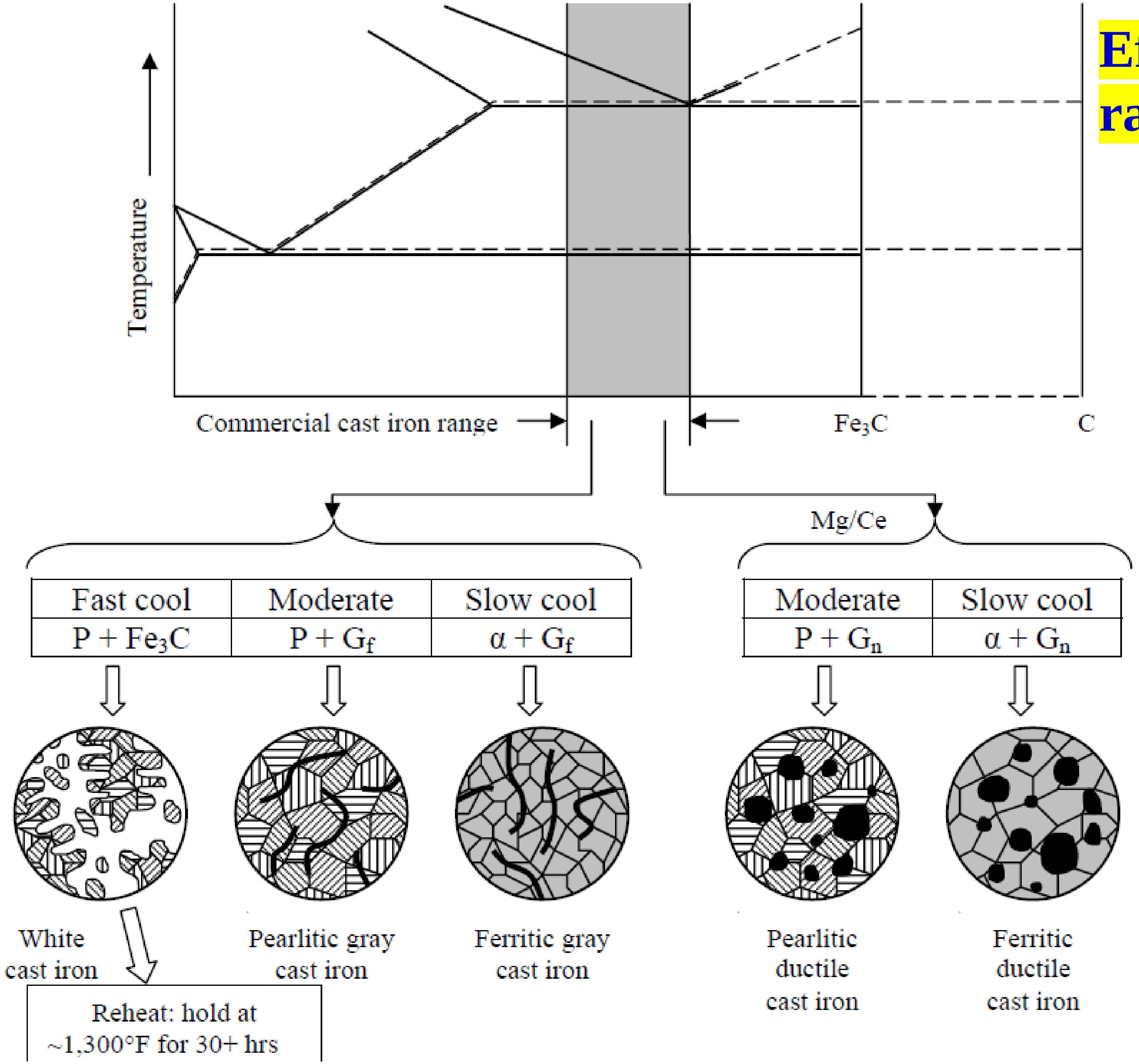
Factors affecting

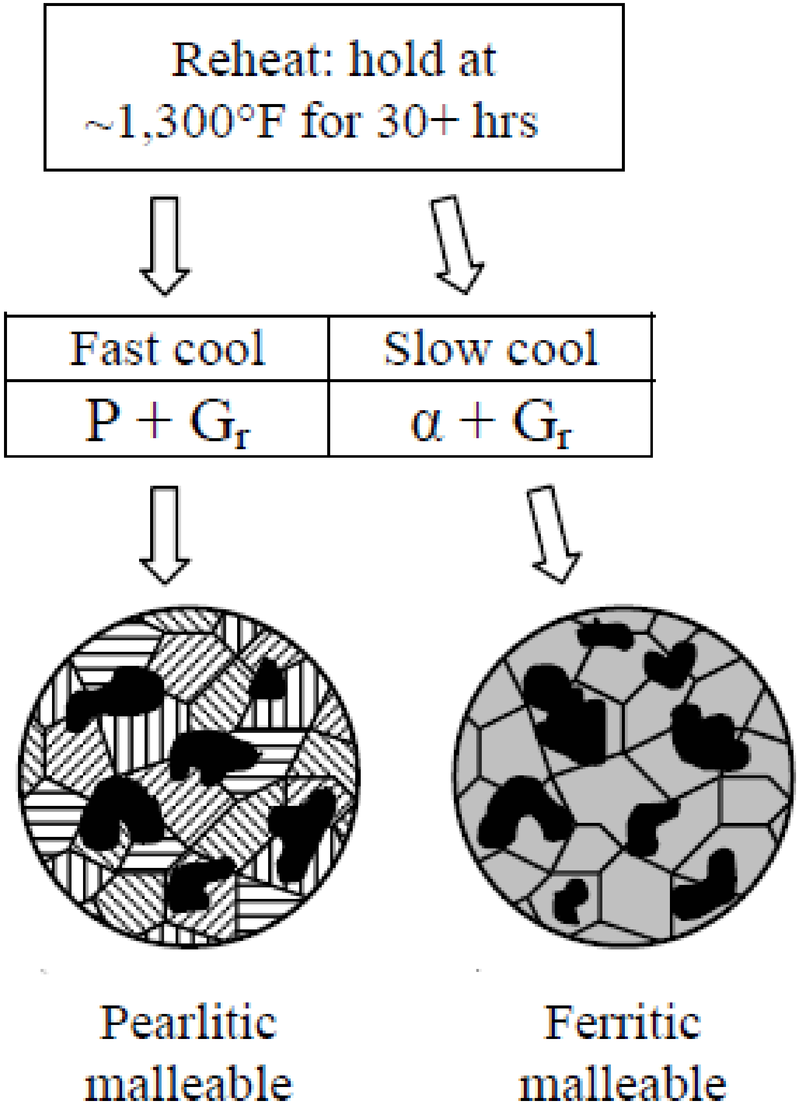
1. Chemical composition
   - Carbon Equivalent CE **for Cast Iron:**

     CE value = %C + 1/3 (%Si + %P)

   - Additives
2. Rate of cooling
   - gray or white
   - matrix control (ferritic, pearlitic or ferritic pearlitic)
3. Liquid treatment:
   - Inoculation
   - spheroidizing
4. Heat treatment
   - Malleablizing HT
   - ADI HT

Effect of cooling rate:





Effect of cooling rate:

- **Phase stability**
  - **- Gray iron produced by slow cooling of liquid iron**
  - **- White iron produced by a relatively higher cooling rate**
- **Matrix constituents**
  - **Ferritic matrix**
  - **Pearlitic**
  - **Ferritic pearlitic**

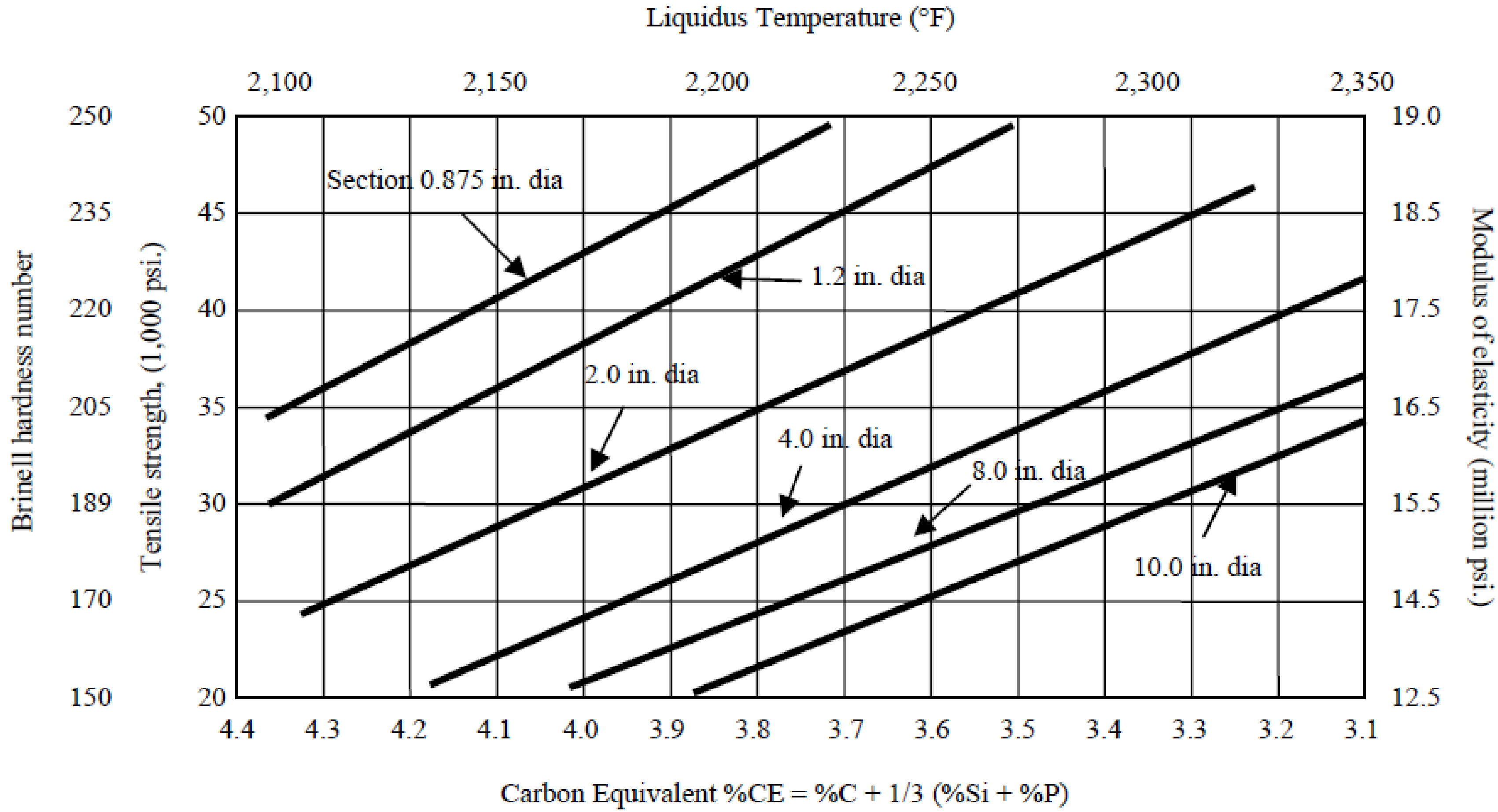
Table 1.1: The typical chemical composition of each type of cast iron (Prasertsakul).

Type of Cast Iron	wt% C	wt% Si	wt% Mn	wt% P	wt% S	wt% Cr
Gray cast iron	2.5 – 4.0	3.0 – 1.0	0.5 – 1.4	0.05 – 0.20	< 0.2	-
Ductile (nodular) cast iron	2.5 – 4.5	4.0 – 1.2	0.3 – 0.8	< 0.05	< 0.03	Mg 0.02 – 0.07
Blackheart malleable cast iron	2.0 – 2.9	1.5 – 0.8	< 0.4	< 0.2	< 0.2	-
Whiteheart malleable cast iron	2.8 – 3.2	1.11 – 0.60	< 0.5	< 0.2	< 0.3	< 0.15
Pearlitic malleable cast iron	2.0 – 2.6	1.5 – 1.0	0.2 – 1.1	< 0.2	< 0.2	< 0.08

Effect of chemical composition:

- **High CE (high carbon & silicon) → Gray iron**
- **Low CE → white iron**

Effect of cooling rate and chemical composition:

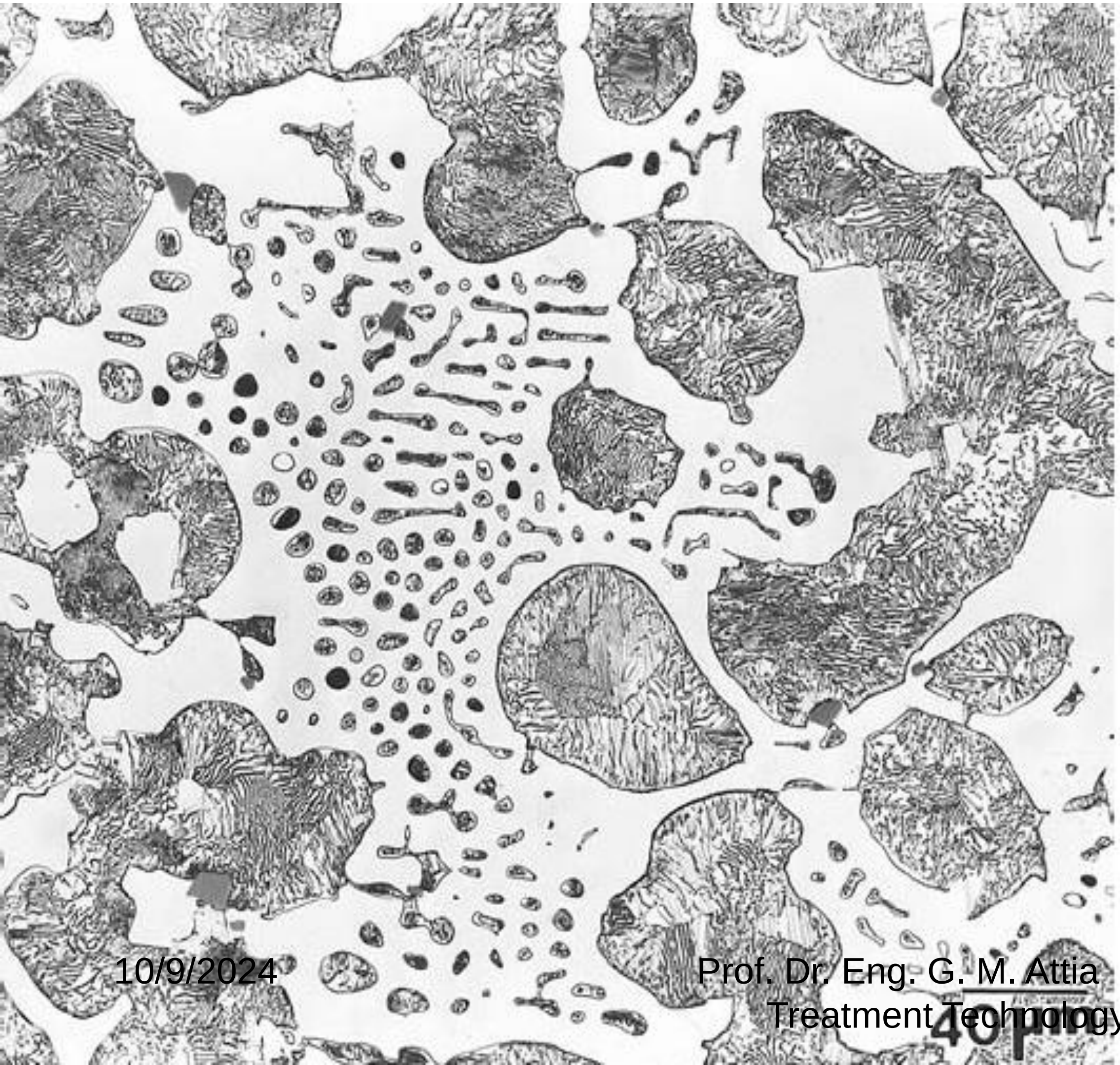


The relationships between the thickness or diameter (cooling rate) of the casting, mechanical properties, and the liquidus temperature of the cast iron with the percent Carbon Equivalent.

White Iron

White Cast Iron

- All C as Fe_3C (Cementite)
- Microstructure → Pearlite + Ledeburite + Cementite



Micrograph of a white cast iron showing a microstructure consisting of pearlite (gray etching constituent), cementite (light etching constituent), and ledeburite (regions of rounded clusters). Etched in 4% picral. 250

- ***White Iron***
- If a gray iron is **solidified rapidly**, white iron results. Graphite flakes are not present in white iron. Instead of graphite flakes, an **iron carbide** network forms that gives the white appearance on the fracture surface. The microstructure of a typical white iron is shown in the following Fig.
- The composition range of elements in unalloyed white iron are:
- **C 1.8-3.6, Si 0.5-1.9, Mn 0.25-0.8, P 0.06-0.2, S 0.06-0.2**

White Cast Irons

- White cast irons form eutectic cementite during solidification.
- The white iron microstructure is due to fast solidification rates and alloying that promotes eutectic carbide formation.
- White irons typically have low ductility, high hardness and great wear resistance.
- White irons get their name from the shininess of their crystalline fractures in comparison to the dull gray fractures of graphite irons.

White cast iron

- Production (Low CE, higher cooling rate, addition of carbide forming elements)
- Carbon present as carbide
- Micro structure (Fe_3C + pearlite)
- Hard, brittle, unmachineable
- Shows a “white” crystalline fractured surface
- Excellent wear and abrasion resistance.
- High compressive stress

Malleable Iron

- **Properties and uses of malleable cast irons:** Malleable irons exploit the **excellent casting properties** of cast iron during the casting process, after which they are converted by heat treatment processes into a composition and structure whose **properties resemble that of low-carbon steel.**
- This results in castings that are stronger and much less brittle than ordinary cast irons and are **widely used in** the **automobile, agricultural machinery, and machine tool industries** for the manufacture of small and medium-sized stressed components. Malleable iron castings are also used in the electrical industry for conduit fittings, switch gear cases, and components.

Malleable iron

1. *Black-heart process:*

- In this process the white iron castings are heated in **airtight boxes out of contact with air at 850-950°C for 50-170 hours**, depending upon the mass and thickness of the castings.
- The effect of this prolonged heating is to break down the iron carbide (cementite) of the white cast iron into small **rosettes of graphite (temper graphite)**.
- The name 'black-heart' comes from the darkened appearance of the iron, when fractured, resulting from the formation of free graphite. **It is used in** the wheel hubs, brake drums, **conduit fitting**, control levers, and pedals.

Malleable iron

2. White-heart process:

- In this process the castings are packed into **airtight boxes with iron oxide in the form of high-grade ore. They are then heated to about 1000°C for between 70 and 100 hours**, depending upon the mass and thickness of the castings.
- **The ore oxidizes the carbon in the castings** and draws it out, **leaving a ferritic structure near the surface and a pearlitic structure near the center** of the casting.
- There will also be some fine rosettes of graphite. White-heart castings behave much as expected of a **mild steel casting** but with the advantage of a very much lower melting point and higher fluidity at the time of casting.

Malleable iron

3. Pearlitic process:

- This process is similar **to the black-heart** process inasmuch as the castings are heated to 850-950°C for 50-170 hours in a non-oxidizing environment.
- As in the black-heart process, the iron carbide (cementite) breaks down into austenite and free graphite. **However, in the pearlitic cast iron process, rapid cooling prevents the austenite from changing into ferrite and graphite,** and a pearlitic structure is produced instead.
- Since this 'pearlitic cast iron' also **has a fine grain resulting from the rapid cooling**, it is harder, tougher, and has a higher tensile strength than black-heart cast iron. However, there is a marked reduction in malleability and ductility.
- Pearlitic malleable irons can be produced by increasing the **manganese content** of the melt from 1.0 to 1.5 percent. This inhibits the production of free graphite and encourages the formation of cementite and pearlite. It is used in gears, couplings, axle housing, differential housing, and components.

Malleable Cast Iron

$$\text{White Cast Iron} \xrightarrow[\text{To Increase Ductility}]{\text{Malleabilize}} \text{Malleable Cast Iron}$$

$$Fe_3C \text{ (WCI)} \xrightarrow[\text{2 stage heat treatment}]{>48\,hrs} \text{Graphite Temper Nodules (Malleable Iron)}$$

Stage I

- (940-960)°C *(Above eutectoid temperature)*
- Competed when all Cementite → Graphite

A: Low T structure (Ferrite + Pearlite + Martensite) → (γ + Cementite)

B: Graphite nucleation at γ/Cementite interface
(rate of nucleation increased by C, Si)
(Si ↓ solubility of C in γ ⇒ ↑ driving force for growth of Graphite)

C: Cementite dissolves → C joining growing Graphite plates

Time for Graphitization in Stage I

- Spacing between Cementite and Graphite →
  ↓ *spacing* ⇒ ↓ *time (obtained by faster cooling of liquid)*
- Addition of Alloying elements
  → *which increase the nucleation rate of Graphite temper nodules*
- Si ↑ ⇒ t ↓

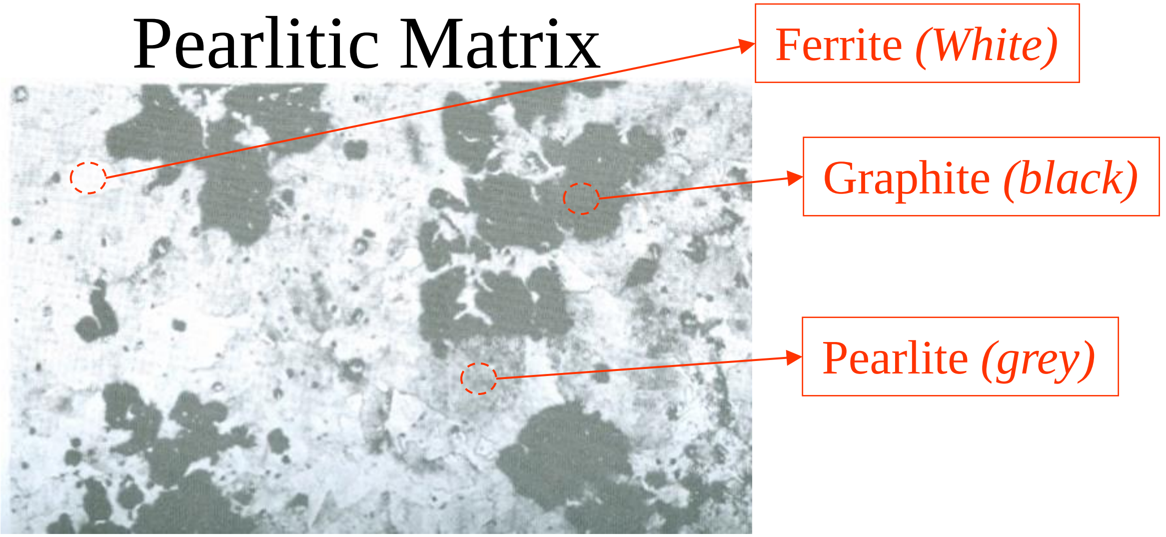
Stage II

- (720-730)°C *(Below eutectoid temperature)*
- After complete graphitization in Stage I → Further Graphitization

- Slow cool to the lower temperature such that γ does not form Cementite
- C diffuses through γ to Graphite temper nodules
  (called Ferritizing Anneal)
- *Full* Anneal in Ferrite + Graphite two phase region
- *Partial* Anneal *(Insufficient time in Stage II Graphitization)*
  $\gamma \rightarrow$ Ferrite is partial and the remaining γ transforms to Pearlite
  $\Rightarrow \gamma \rightarrow$ Pearlite + Ferrite + Graphite
- If quench after Stage I $\Rightarrow \gamma \rightarrow$ Martensite *(+ Retained Austenite(RA))*
  (Graphite temper nodules are present in a matrix of Martensite and RA)

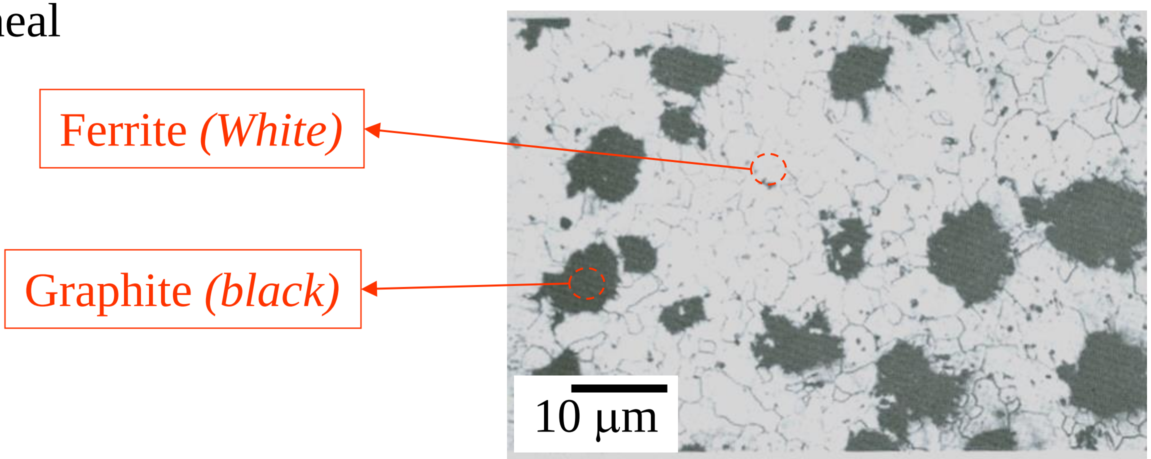
Malleable Iron

Pearlitic Matrix



Partially Malleabilized Iron
→ Incomplete Ferritizing Anneal

Ferritic Matrix



Fully Malleabilized Iron
→ Complete Ferritizing Anneal

Growth of Graphite

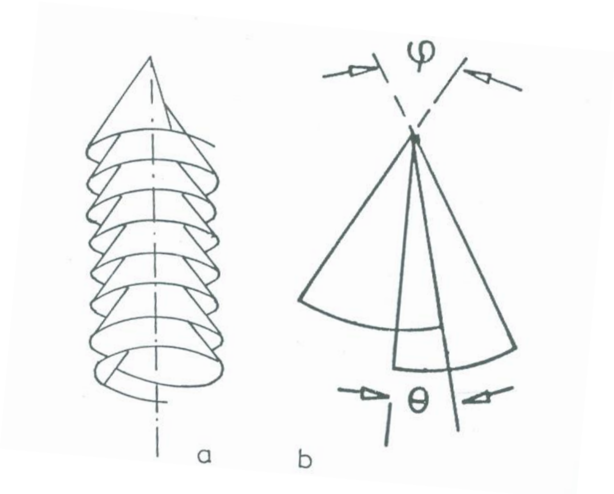
Hillert and Lidblom

Growth of Graphite from Screw dislocations

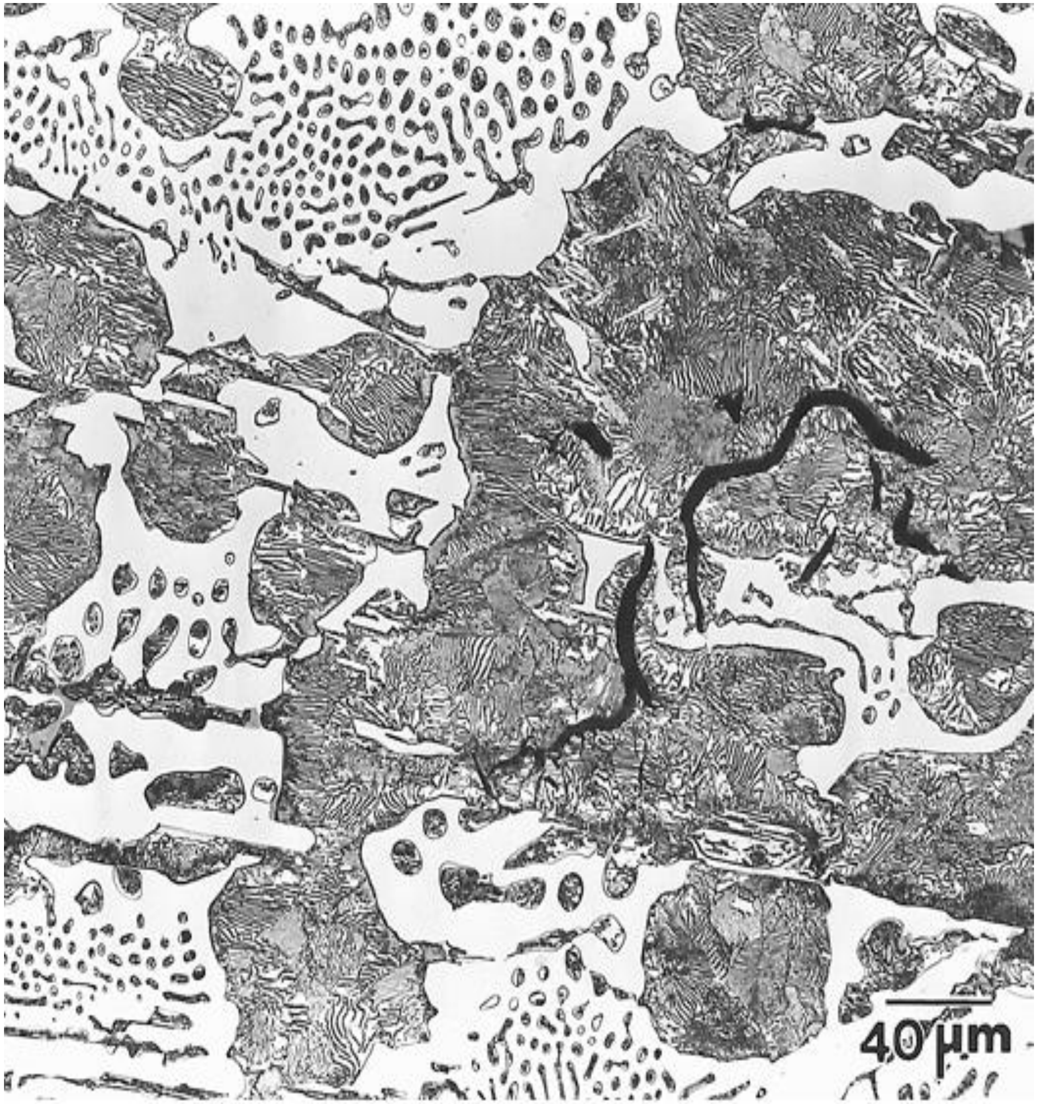
Growth of Graphite

Hunter and Chadwick

Double and Hellawell



- **Mottled Iron.**
- **This type of cast iron is not intentionally produced.**
- It results from a transition between gray and white iron in casting and is not necessarily a desirable material.
- The microstructure of a mottled iron is shown in the following figure.



Micrograph of a **mottled cast** iron showing a microstructure consisting of pearlite (dark gray etching constituent), cementite (light etching constituent), ledeburite (clusters of small, rounded pearlite particles), and graphite flakes (dark constituent). Etched in 4% picral. **250X**

Grey Cast Iron

Chemical composition

$\in$ [2.4% (for good castability), 3.8 (for OK mechanical propeties)]

< 1.25% → Inhibits graphitization

< 0.1% → retards graphitization; ↑ size of Graphite flakes

- Fe-C-Si + (Mn, P, S)
  → *Invariant lines become invariant regions in phase diagram*
- Si $\in$ (1.2, 3.5) → C as Graphite flakes in microstructure (Ferrite matrix)

↑ volume during solidification ⇒ better castability

$$\mathrm{L} \rightarrow \underbrace{\gamma + (Fe_3C)}_{Ledeburite} \rightarrow \underbrace{\alpha + Fe_3C}_{Pearlite} + (Fe_3C)$$

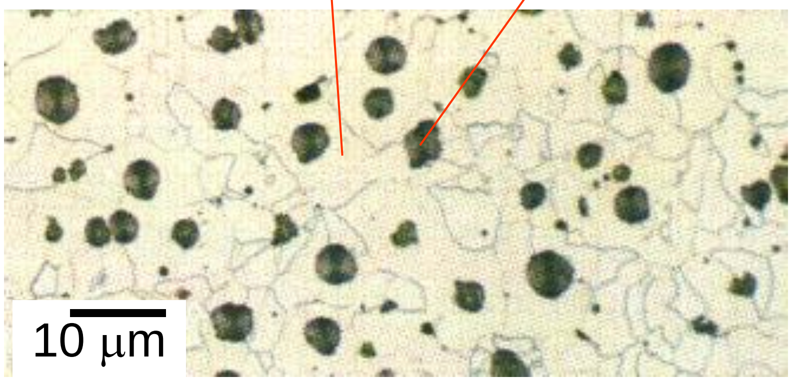
Si ↑ ⇒ $\overleftarrow{C_{eutectoid}}$

- Si decreases Eutectivity
- Si promotes graphitization → ~ effect as ↓ cooling rate
- Solidification over a range of temperatures permits the nucleation and growth of Graphite flakes
- Change in interfacial energy between γ/L & Graphite/L brought about by Si
- Growth of Graphite along ‘a’ axis

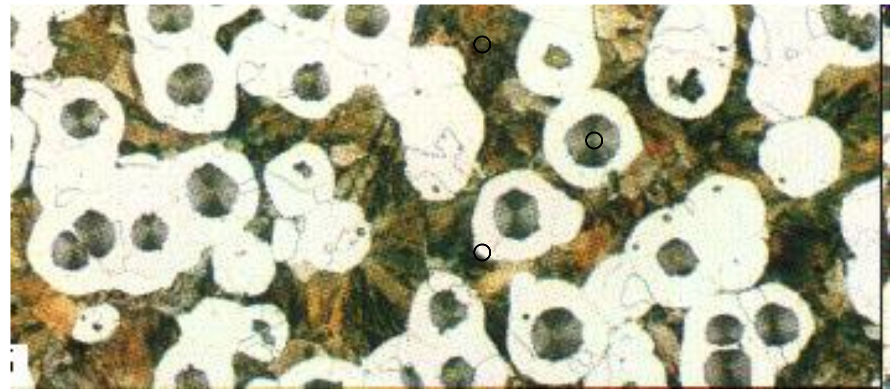
Ductile/Spheroidal Cast Iron

- Graphite nodules instead of flakes *(in 2D section)*
- Mg, Ce, Ca (or other spheroidizing) elements are added
- The elements added to promote spheroidization react with the solute in the liquid to form heterogenous nucleation sites
- The alloying elements are injected into mould before pouring *(George-Fischer container)*
- It is thought that by the modification of the interfacial energy the ‘c’ and ‘a’ growth direction are made comparable leading to spheroidal graphite morphology
- The graphite phase usually nucleates in the liquid pocket created by the proeutectic γ

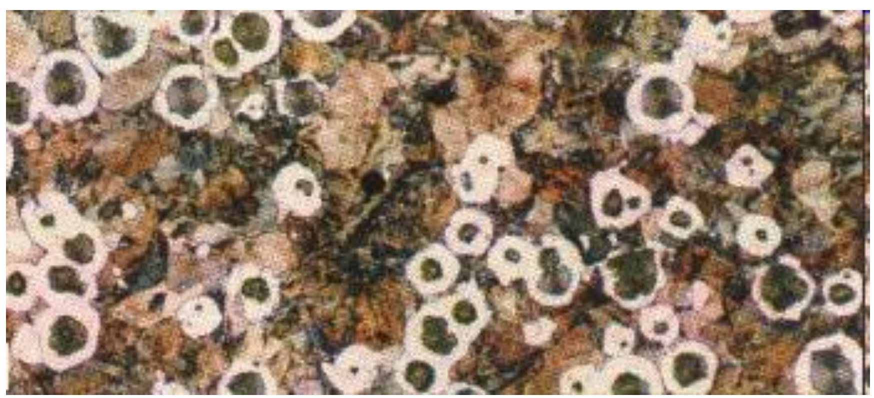
Ductile Iron/Nodular Iron



With Ferritic Matrix

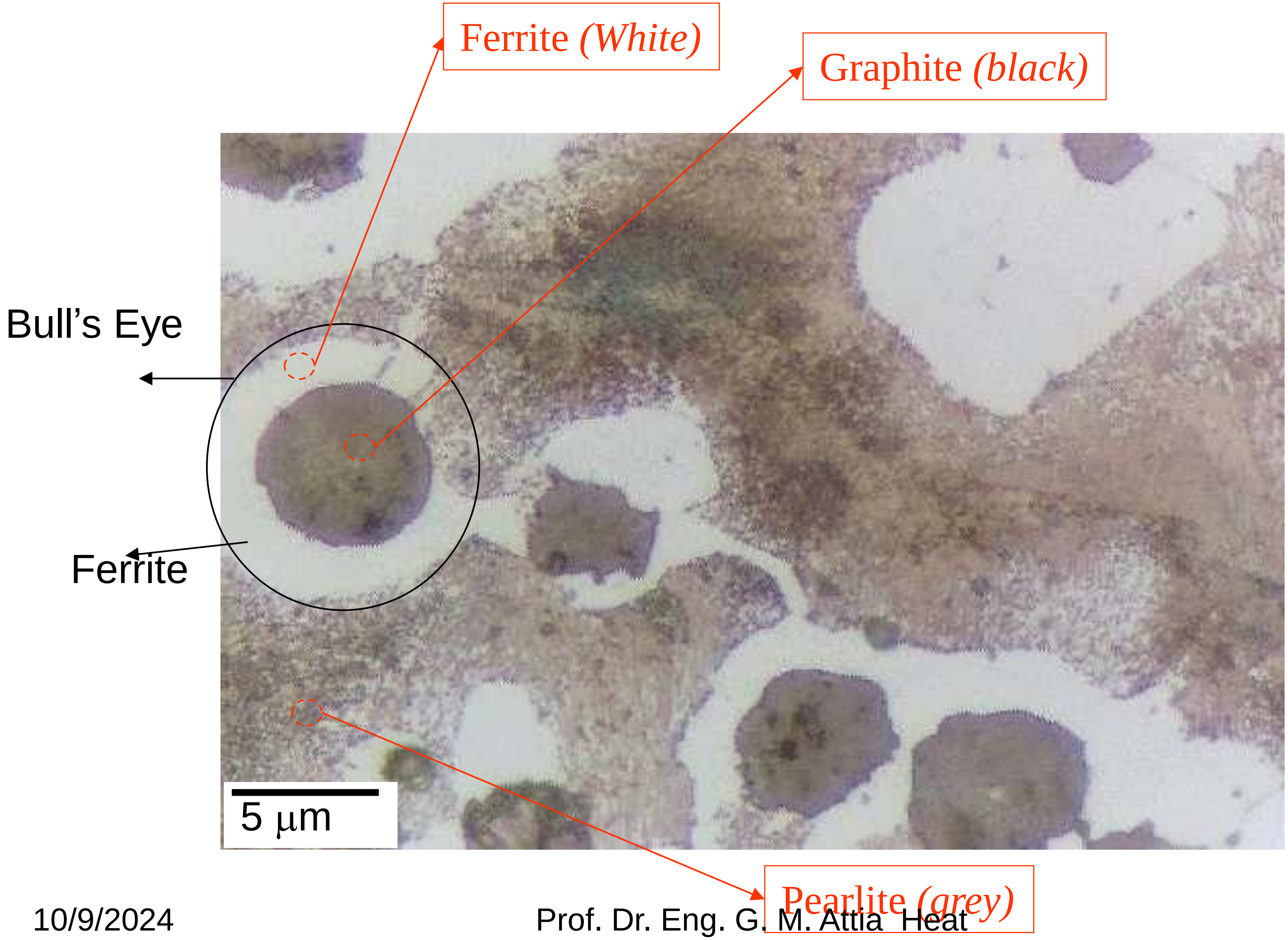


With (Ferrite + Pearlite) Matrix



With Pearlitic matrix

Ductile Iron/Nodular Iron



Alloy Cast Irons

- Cr, Mn, Si, Ni, Al
- ↑ the range of microstructures
- Beneficial effect on many properties
  - ↑ high temperature oxidation resistance
  - ↑ corrosion resistance in acidic environments
  - ↑ wear/abaration resistance

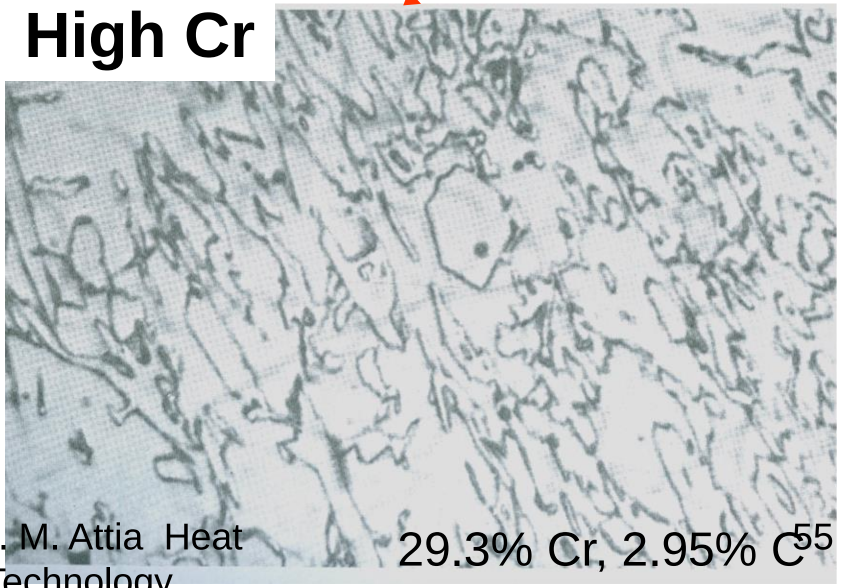
Alloy Cast Irons
→ Graphite free
→ Graphite bearing

Cr addition (12- 35 wt %)

- Excellent resistance to oxidation at high temperatures
- High Cr Cast Irons are of 3 types:

- 12-28 % Cr ➢ matrix of Martensite + dispersed carbide
- 29-34 % Cr ➢ matrix of Ferrite + dispersion of alloy carbides $[(Cr,Fe)_{23}C_6, (Cr,Fe)_7C_3]$
- 15-30 % Cr + 10-15 % Ni ➢ stable γ + carbides $[(Cr,Fe)_{23}C_6, (Cr,Fe)_7C_3]$ *Ni stabilizes Austenite structure*

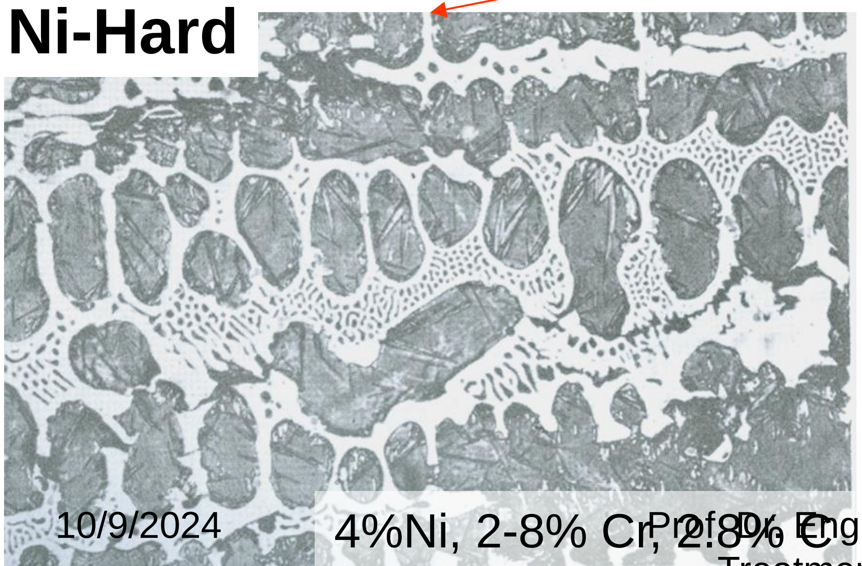
High Cr



29.3% Cr, 2.95% C

- **Ni:**
- Stabilizes Austenitic structure
- ↑ Graphitization *(suppresses the formation of carbides)*
- (Cr counteracts this tendency of Ni for graphitization)
- ↓ Carbon content in Eutectic
- Moves nose of TTT diagram to higher times ⇒ easy formation of Martensite
- Carbide formation in presence of Cr increases the hardness of the eutectic structure → Ni Hard Cast Irons (4%Ni, 2-8% Cr, 2.8% C)

Ni-Hard



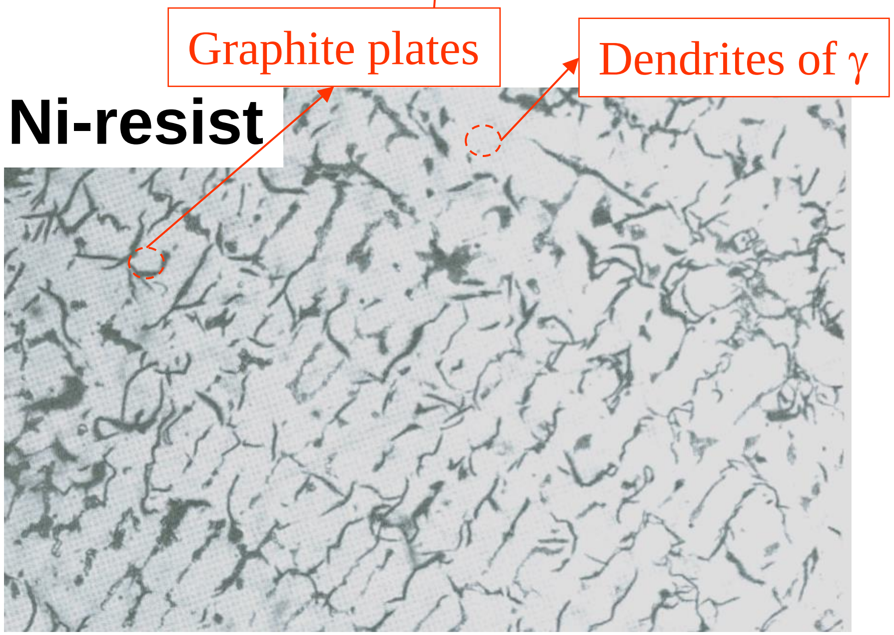
4%Ni, 2-8% Cr, 2.8% C

Good abrasion resistance

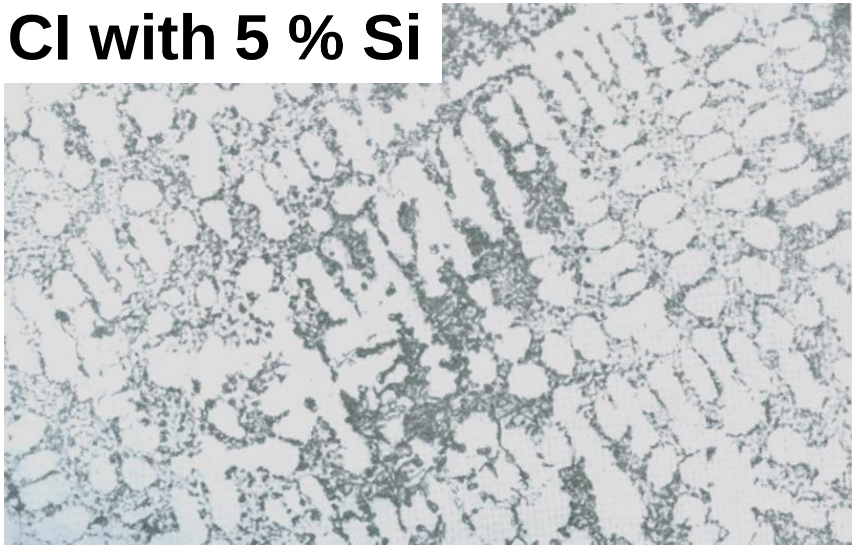
Needles of Martensite

Transformation sequence
- Crystallization of primary γ
- Eutectic liquid → γ + alloy carbide
- γ → Martensite

- Ni Resist Iron: 15-30% Ni + small amount of Cr:
- Austenitic Dendrites + Graphite plates/flakes + interdendritic carbides due to presence of Cr
- Resistant to oxidation (used in chemical processing plants, sea water, oil handling operations…)



- Silal Iron (trade name): Alloy CI with 5% Si
- Si allows solidification to occur over larger temperature range → promotes graphitization
- Forms surface film of iron silicate → resistant to acid corrosion



CI with 5 % Si

TABLE 12-5 *Typical properties of cast irons*

	Tensile Strength (psi)	Yield Strength (psi)	% E	Notes
Gray irons:				
Class 20	12,000–40,000	—	—	
Class 40	28,000–54,000	—	—	
Class 60	44,00–66,000	—	—	
Malleable irons:				
32510	50,000	32,500	10	Ferritic
35018	53,000	35,000	18	Ferritic
50005	70,000	50,000	5	Pearlitic
70003	85,000	70,000	3	Pearlitic
90001	105,000	90,000	1	Pearlitic
Ductile irons:				
60–40–18	60,000	40,000	18	Annealed
65–45–12	65,000	45,000	12	As-cast ferritic
80–55–06	80,000	55,000	6	As-cast pearlitic
100–70–03	10,000	70,000	3	Normalized
120–90–02	120,000	90,000	2	Quenched and tempered
Compacted graphite irons:				
Low strength	40,000	28,000	5	90% Ferritic
High strength	65,000	55,000	1	80% Pearlitic

Property	Gray iron GG Type			
	GG10	GG20	GG30	GG40
Tensile N/mm2	100	200	300	400
Compressive	500 - 600	600 - 800	800 - 1200	1100 - 1400
HB	100 -150	170 - 210	200 - 260	230 - 300
Property	Malleable iron GTW Type			
	GTW 35	GTW 40	GTW 45	GTW 55
Tensile N/mm2	350	400	450	550
Elongation%	4	5	7	5
HB	< 220	< 200	< 200	< 240
Yield	200	220	260	360
Property	Ductile iron GGG Type			
	GGG 40	GGG 50	GGG 60	GGG 70
Tensile N/mm2	400	500	600	700
Elongation%	15	7	3	2
HB	135 - 185	170 – 220	200 – 250	235 - 285
Yield	250	320	380	440

End