



Metallurgical Aspects of HIGH- CHROMIUM WHITE IRONS

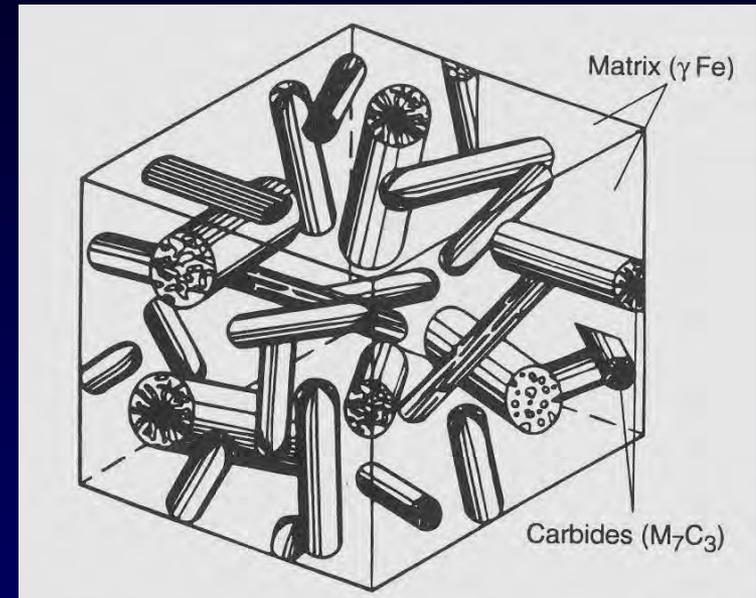
PROF. DR. ADEL NOFAL
CMRDI – Cairo Egypt

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- ❖ **The high-chromium white irons have excellent abrasion resistance and are used effectively in slurry pumps, brick molds, coal grinding mills, shot blasting equipment, and components for quarrying, hard-rock mining, and milling. In some applications they must also be able to withstand heavy impact loading.**
 - ❖ **These alloyed white irons provide the best combination of toughness and abrasion resistance attainable among the white cast irons.**
 - ❖ **In the high-chromium irons, as with most abrasion-resistant materials, there is a tradeoff between wear resistance and toughness.**
 - ❖ **By varying composition and heat treatment, these properties can be adjusted to meet the needs of most abrasive applications.**

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- ❖ As a class of alloyed irons, the high-chromium irons are distinguished by the hard, relatively discontinuous M_7C_3 eutectic carbides present in the microstructure, as opposed to the softer, more continuous M_3C eutectic carbides present in the alloyed irons containing less chromium.
 - ❖ These alloys are usually produced as hypoeutectic compositions. The randomly oriented bundles/rods of carbide embedded in the metallic matrix are evident.
 - ❖ In an idealized cube of high Cr-white iron, the randomly oriented rods of carbide embedded in the metallic matrix are shown.

INTRODUCTION

- ❖ The high-alloy white irons are primarily used for abrasion-resistant applications and are readily cast in the shapes needed in the machinery used for crushing, grinding, and general handling of abrasive materials.
- ❖ The large volume of eutectic carbides in their microstructures provides the high hardness needed for crushing and grinding other materials.
- ❖ The metallic matrix supporting the carbide phase in these irons can be adjusted by alloy content and heat treatment to develop the proper balance between resistance to abrasion and the toughness needed to withstand repeated impact.



Schematic showing the heterogeneous microstructure of high-chromium white irons.

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- ❖ **All high-alloy white irons contain chromium to prevent formation of graphite on solidification and to ensure the stability of the carbide phase.**
 - ❖ **Most also contain nickel, molybdenum, copper, or combinations of these alloying elements to prevent the formation of pearlite in the microstructure.**
 - ❖ **White low-alloyed pearlitic white iron castings develop hardness in the range 350 to 550 HB, the hardness of high-alloyed white irons ranges from 450-800 HB.**

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- ❖ In addition, several grades contain alloy eutectic carbides (M_7C_3 chromium carbides) that are substantially harder than the iron carbide in low-alloy irons.
 - ❖ For many applications, the increased abrasion resistance of the more expensive high-alloy white irons adds significantly to wear life, causing them to provide the most cost-effective performance.

ALLOY GRADES AND SPECIFICATIONS

- ❖ **ASTM specifications A532 covers the composition and hardness of white irons grades used for abrasion-resistant applications.**
- ❖ **Many castings are ordered according to these specifications; however, a large number of castings are produced with modifications to composition for specific applications.**
- ❖ **It is most desirable that the designer, metallurgist, and foundry worker cooperate to specify the composition, heat treatment, and foundry practice to develop the most suitable alloy and casting design for a specific applications.**

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- ❖ **The high-alloy white cast irons fall into three major groups:**
 - ❖ **The nickel-chromium white irons, which are low-chromium alloys containing 3 to 5% Ni and 1 to 4% Cr, with one alloy modification which contains 7 to 11% Cr. They are commonly identified by the trade name Ni-Hard types 1 to 4.**
 - ❖ **The chromium-molybdenum irons, which contain 11 to 23% Cr and up to 3% Mo, and are often additionally alloyed with nickel or copper.**
 - ❖ **The 25% Cr or 28% Cr white irons, which may contain other alloying additions of molybdenum and/or nickel up to 1.5%.**
 - ❖ **This presentation is restricted to high-Cr white irons.**

Composition and hardness requirements of abrasion-resistant white irons per ASTM A 532

Class	Type	Designation	Composition, wt %								
			C	Mn	Si	Ni	Cr	Mo	Cu	P	S
I	A	Ni-Cr-HiC	2.8-3.6	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	...	0.3 max	0.15 max
I	B	Ni-Cr-LoC	2.4-3.0	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	...	0.3 max	0.15 max
I	C	Ni-Cr-GB	2.5-3.7	2.0 max	0.8 max	4.0 max	1.0-2.5	1.0 max	...	0.3 max	0.15 max
I	D	Ni-HiCr	2.5-3.6	2.0 max	2.0 max	4.5-7.0	7.0-11.0	1.5 max	...	0.10 max	0.15 max
II	A	12% Cr	2.0-3.3	2.0 max	1.5 max	2.5 max	11.0-14.0	3.0 max	1.2 max	0.10 max	0.06 max
II	B	15% Cr-Mo	2.0-3.3	2.0 max	1.5 max	2.5 max	14.0-18.0	3.0 max	1.2 max	0.10 max	0.06 max
II	D	20% Cr-Mo	2.0-3.3	2.0 max	1.0-2.2	2.5 max	18.0-23.0	3.0 max	1.2 max	0.10 max	0.06 max
III	A	25% Cr	2.0-3.3	2.0 max	1.5 max	2.5 max	23.0-30.0	3.0 max	1.2 max	0.10 max	0.06 max

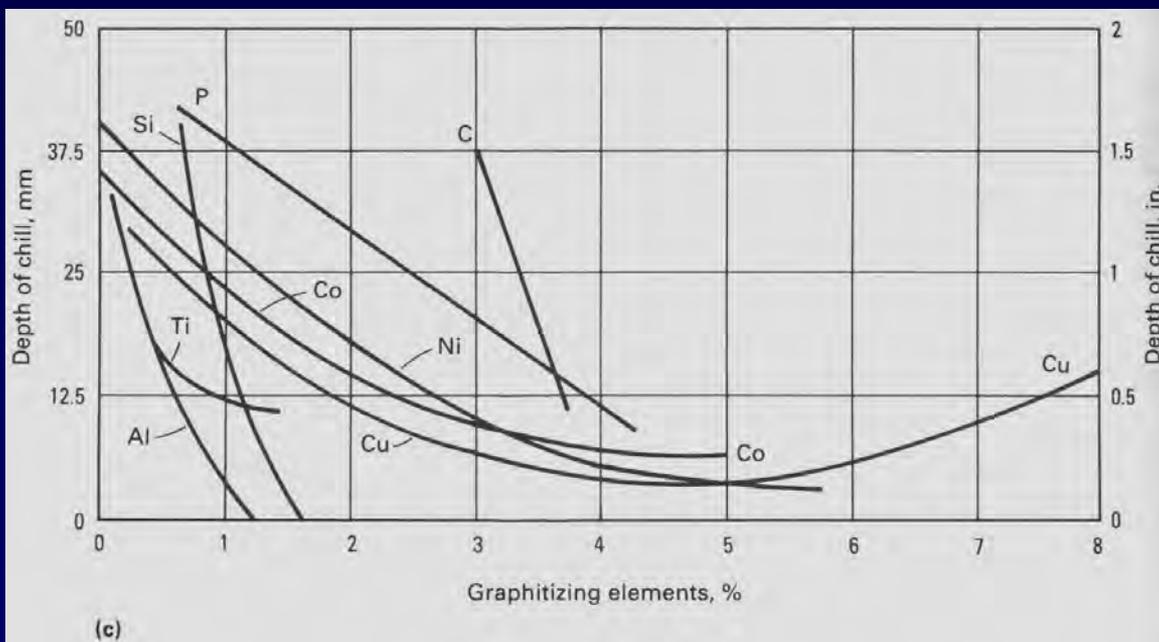
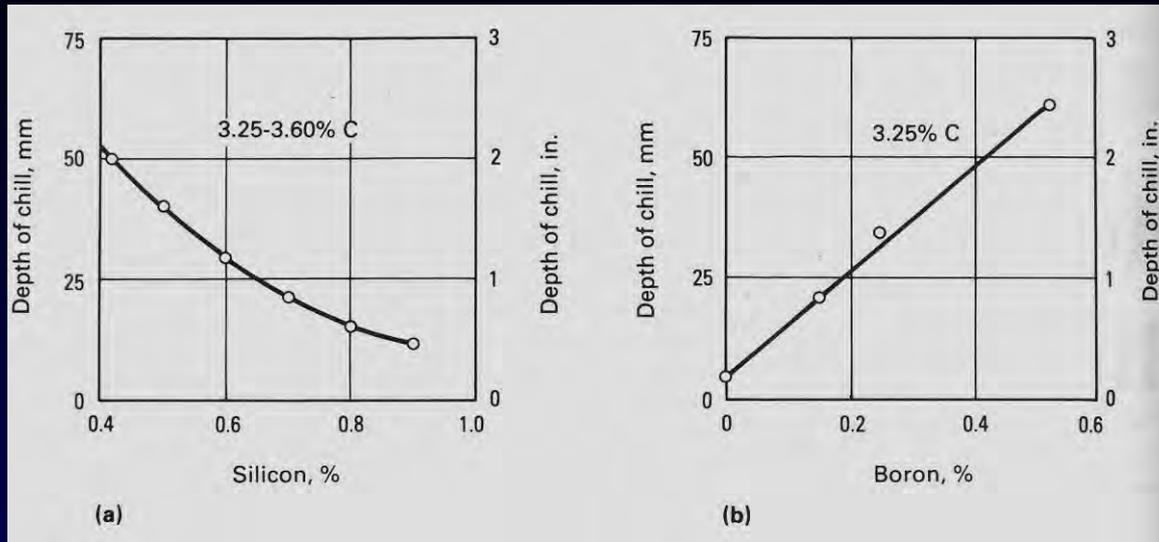
Class	Type	Designation	Hardness value																	
			Sand cast, min(a)			Hardened or hardened and stress relieved									Chill cast, min(b)			Softened, max		
			As-cast or As-cast and stress relieved			Level 1			Level 2			Chill cast, min(b)			Softened, max					
			HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV			
I	A	Ni-Cr-HiC	550	53	600	600	56	660	650	59	715	600	56	660			
I	B	Ni-Cr-LoC	550	53	600	600	56	660	650	59	715	600	56	660			
I	C	Ni-Cr-GB	550	53	600	600	56	660	650	59	715	600	56	660	400	41	430			
I	D	Ni-HiCr	500	50	540	600	56	660	650	59	715	550	53	600			
II	A	12% Cr	550	53	600	600	56	660	650	59	715	550	53	600	400	41	430			
II	B	15% Cr-Mo	450	46	485	600	56	660	650	59	715	400	41	430			
II	D	20% Cr-Mo	450	46	485	600	56	660	650	59	715	400	41	430			
III	A	25% Cr	450	46	485	600	56	660	650	59	715	400	41	430			

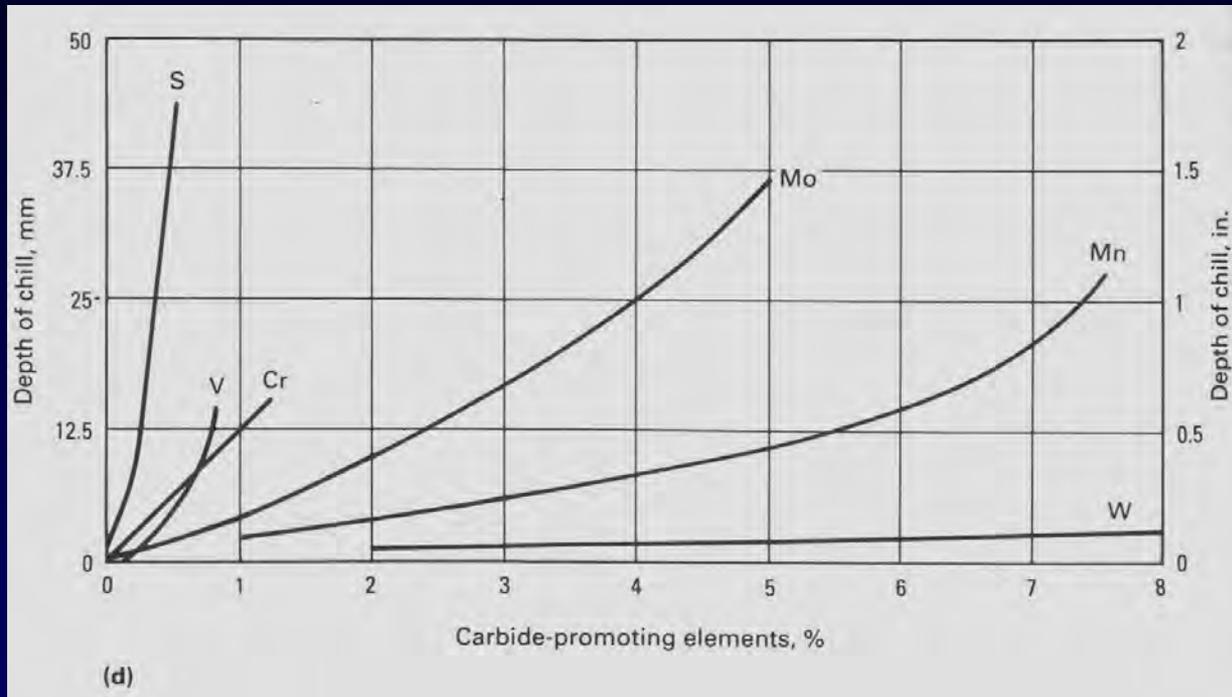
(a) 90% of the minimum surface hardness level shall be maintained to a depth of 40% of the casting section, with any softer material being at the thermal center of the casting. A sampling procedure should be established by agreement between the supplier and the purchaser. (b) Non-chilled areas of casting shall meet minimum hardness or sand cast requirements.

EFFECTS OF ALLOYING ELEMENTS

i) Chromium

- ❖ has three major uses in cast irons
 - to form carbides
 - to impart corrosion resistance
 - to stabilize the structure for high temperature applications
- ❖ at low Cr-contents (<2-3%), Cr has little or no effect on hardenability, as most of Cr is tied up in carbides
- ❖ at Cr-contents more than 10%, eutectic carbides of the M_7C_3 type are formed, rather than the M_3C type. The M_7C_3 are discontinuous and surrounded by the austenite matrix or its transformation products.
- ❖ Hypoeutectic irons containing M_7C_3 carbides are normally stronger and tougher than irons containing M_3C carbides.
- ❖ Martensitic or austenitic white irons containing 12-28% Cr usually contain Mo, Ni, Mn and/or copper to give the required hardenability and ensure martensite formation upon cooling from above the upper transformation temperature, either while the casting is cooling in the mold or during subsequent heat treatment.





Typical effects of alloying elements on depth of chill.

ii) Nickel

- ❖ When added to low-chromium white iron in amounts up to about 2.5%, nickel produces a harder and finer pearlite in the structure, which improves its abrasion resistance.
- ❖ Nickel in somewhat larger amounts, up to about 4.5%, is needed to completely suppress pearlite formation, thus ensuring that a martensitic iron results when the castings cool in their molds. This latter practice forms the basis for production of the Ni-Hard cast irons.
- ❖ With small castings such as grinding balls, which can be shaken out of the molds white still hot, air cooling from the shakeout temperature will produce the desired martensitic structure even when the nickel content is as low as 2.7%.
- ❖ On the other hand, an excessively high nickel content (more than about 6.5%) will so stabilize the austenite that little martensite, if any, can be formed in castings of any size.
- ❖ Appreciable amounts of retained austenite in Ni-Hard cast irons can be transformed to martensite by refrigerating the castings at -55 to 75°C or by using special tempering treatments.

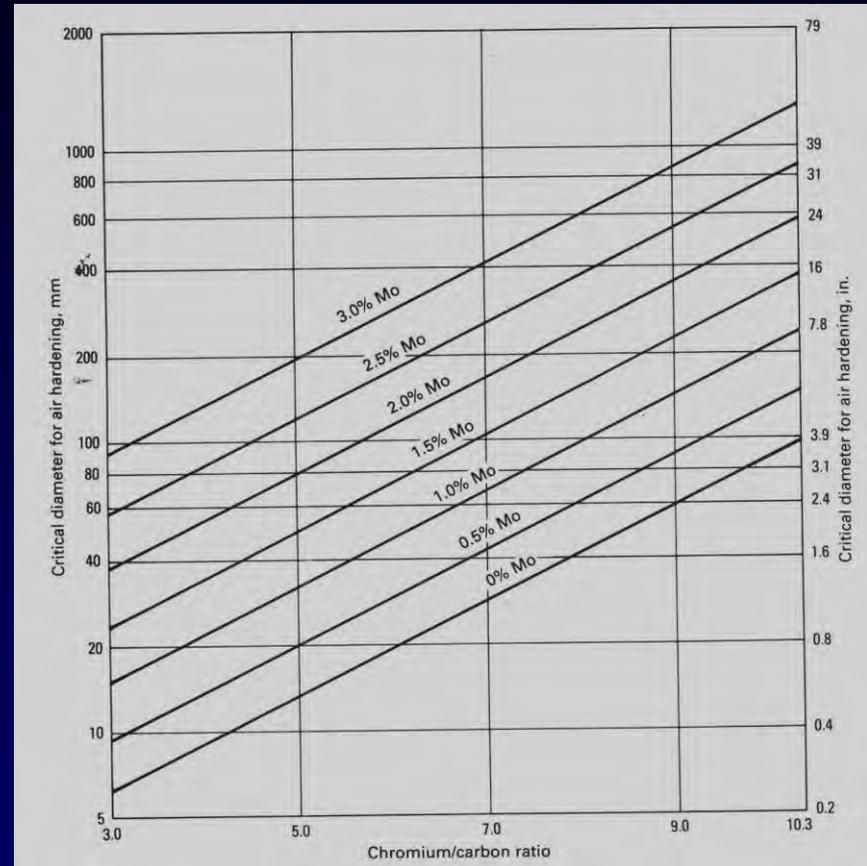
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- ❖ One of the Ni-Hard family of commercial alloy white irons (type IV Ni-Hard) contains 1.0 to 2.2% Si, 5 to 7% Ni, and 7 to 11% Cr. In the as-cast condition, it has a structure of M_7C_3 eutectic carbides in a martensitic matrix.
 - ❖ If retained austenite is present, the martensite content and hardness of the alloy can be increased by refrigeration treatment or by re-austenitizing and air cooling.
 - ❖ Ni-Hard IV is often specified for pumps and other equipment used for handling abrasive slurries because of its combination of relatively good strength, toughness, and abrasion resistance.
 - ❖ Nickel is used to suppress pearlite formation in large castings of high-chromium white iron (12 to 28% Cr). The typical amount of nickel is about 0.2 to 1.5%, and it is usually added in conjunction with molybdenum.
 - ❖ Nickel contents higher than this range tend to excessively stabilize the austenite, leading to austenite retention.
 - ❖ Control of composition is especially important for large castings that are intended to be martensitic, because their size dictates that they cool slowly regardless of whether they are to be used as-cast or after heat treatment.

iii) Copper

- ❖ Copper in moderate amounts can be used to suppress pearlite formation in both low- and high-chromium martensitic white irons. The effect of copper is relatively mild compared to that of nickel, and because of the limited solubility of copper in austenite, copper additions probably should be limited to about 2.5% or less.
- ❖ Copper is most effective in suppressing pearlite when it is used in conjunction with about 0.5 to 2.0% Mo. The hardenability of this combination is surprisingly good, which indicates that there is a synergistic effect when copper and molybdenum are added together to cast iron.
- ❖ Combined additions appear to be particularly effective in the martensitic high-chromium irons. Here, copper content should be held to 1.2% or less; larger amounts tend to induce austenite retention.

iv) Molybdenum

- ❖ When a martensitic white iron is desired for superior abrasion resistance, additions of 0.5 to 3.0% Mo effectively suppress pearlite and other high-temperature transformation products.
- ❖ Molybdenum is even more effective when used in combination with copper, chromium, nickel, or both chromium and nickel.
- ❖ Molybdenum has an advantage over nickel, copper, and manganese in that it increases depth of hardening without appreciably overstabilizing austenite, thus preventing the retention of undesirably large amounts of austenite in the final structure.
- ❖ The hardenability (measured as the critical diameter for air hardening) increases as the ratio of chromium to carbon increases.



Effect of molybdenum content on the hardenability of high-chromium white irons of different Cr/C ratios

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- ❖ The pearlite-suppressing properties of molybdenum have been used to advantage in irons of high chromium content. White irons with 12 to 18% Cr are used for abrasion-resistant castings. The addition of 1 to 4% Mo is effective in suppressing pearlite formation, even when the castings are slowly cooled in heavy sections.
 - ❖ Molybdenum can replace some of the nickel in the nickel-chromium type of martensitic white irons. In heavy-section castings in which 4.5% Ni would be used, the addition of 1% Mo permits a reduction of nickel content to about 3%. In light-section castings of this type, where 3% Ni would normally be used, the addition of 1% Mo permits a reduction of nickel to 1.5%..

NICKEL-CHROMIUM WHITE IRONS

- ❖ The oldest group of high-alloy irons of industrial importance, the nickel-chromium white irons (Ni-Hard irons), have been produced for more than 50 years and are cost-effective materials for crushing and grinding. In these martensitic white irons, nickel is the primary alloying element, because 3 to 5% Ni is effective in suppressing the transformation of the austenite matrix to pearlite, thus ensuring that a hard, martensitic structure (usually containing significant amounts of retained austenite) will develop upon cooling in the mold. Chromium is included in these alloys, at levels from 1.4 to 4% to ensure that the irons solidify carbidic (i.e., to counteract the graphitizing effect of nickel).

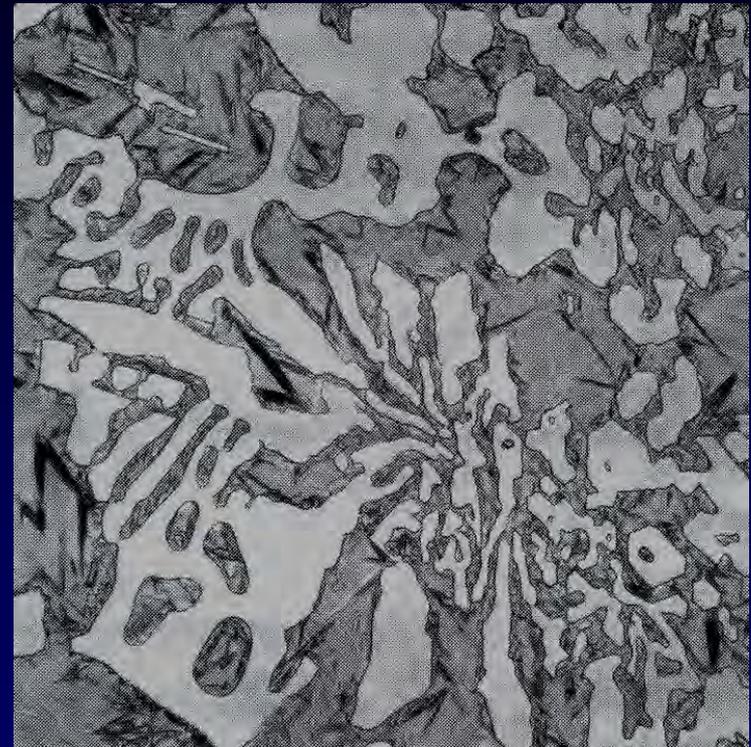


Typical microstructure of class I type A nickel-chromium white cast iron.

Composition Selection and Control

- ❖ **The optimum condition of a nickel-chromium white iron alloy depends on the service conditions and the dimensions and weight of the casting. Abrasion resistance is generally a function of the bulk hardness and the volume of carbide in the microstructure.**
 - i) When abrasion resistance is the principal requirement and resistance to impact loading is secondary, alloys having high carbon contents, ASTM A 532 class I type A (Ni-Hard 1), are recommended.**
 - ii) When conditions of repeated impact are anticipated, the lower-carbon alloys, class I type B (Ni-Hard 2), are recommended because they have less carbide and, therefore, greater toughness.**
 - iii) A special grade, class I type C, has been developed for producing grinding balls and slugs. Here the nickel-chromium alloy composition has been adapted for chill casting and specialized sand casting processes.**

- ❖ The class I type D (Ni-Hard 4) alloy is a modified nickel-chromium iron that contains higher levels of chromium, ranging from 7 to 11% and increased levels of nickel, ranging from 5 to 7%.
- ❖ Whereas the eutectic carbide phase in the lower-alloyed nickel-chromium irons is M_3C (iron carbide), which forms as a continuous network in these irons, the higher chromium in the type D alloy promotes M_7C_3 chromium carbides, which form a relatively discontinuous eutectic carbide distribution.
- ❖ This modification in the eutectic carbide pattern provides an appreciable improvement in resistance to fracture by impact.
- ❖ The higher alloy content of this iron grade also results in improved corrosion resistance, which has proved to be useful in the handling of corrosive slurries.



Typical microstructure of class I type D nickel-chromium white cast iron.

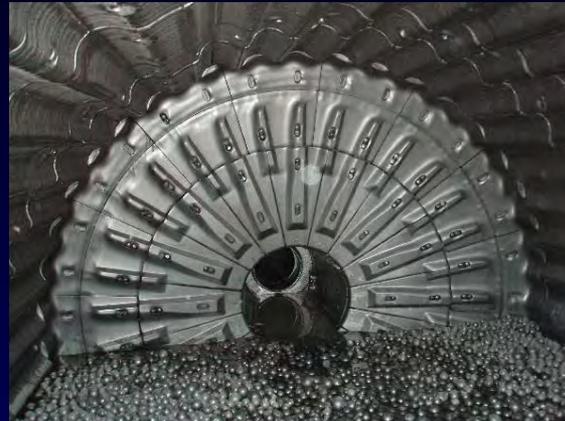
Applications

- ❖ The martensitic nickel-chromium white irons are consumed in large tonnages in mining operations as ball mill liners and grinding balls.
- ❖ *Class I type A* castings are used in applications requiring maximum abrasion resistance, such as ash pipes, slurry pumps, roll heads, muller tires, augers, coke crusher segments, classifier shoes, brick molds, pipe elbows carrying abrasive slurries, and grizzly disks.
- ❖ *Type B* is recommended for applications requiring more strength and exerting moderate impacts, such as crusher plates, crusher concaves, and pulverizer pegs.
- ❖ *Class I type D, Ni-Hard type 4*, has a higher level of strength and toughness and is therefore used for the more severe applications that justify its added alloy costs. It is commonly used for pump volutes handling abrasive slurries and coal pulverizer table segments and tires.
- ❖ *The class I type C alloy (Ni-Hard 3)* is specially designed for the production of grinding balls. This grade is both sand cast and chill cast. Chill casting has the advantage of lower alloy cost, and, more important, provides a 15 to 30% improvement for 8 h at 260 to 315°C.

Examples of Ni-Hard Castings



Ash Pipes



Ball Mill



Classifier Shoes



Crusher Plates



Grinding Balls



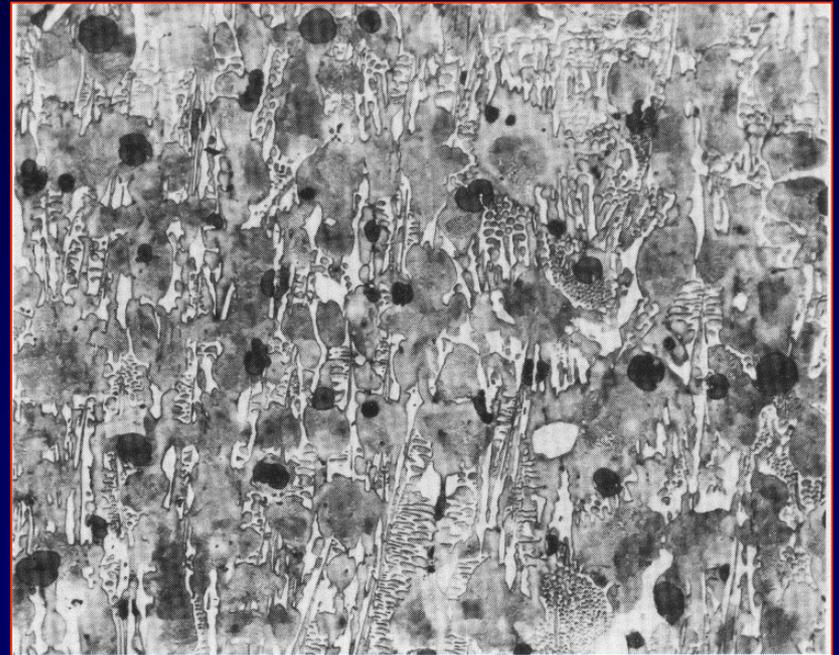
Pipe Elbows



Slurry Pumps

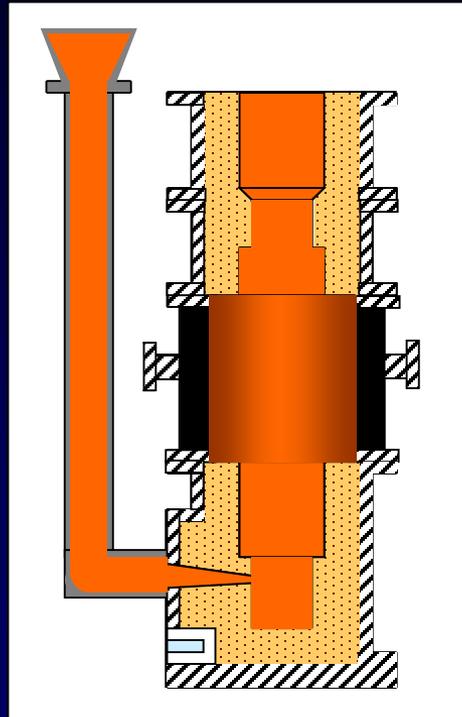
Special Nickel-Chromium White Iron Alloys

- ❖ Certain proprietary grades of type A alloy have been developed by the rolling mill industry. The compositions of these alloys have been modified to produce mottled structures containing some graphite.
- ❖ The graphite inclusions are reported to improve resistance to thermal cracking. These indefinite chill rolls are cast in thick-wall gray iron chiller molds in roll diameters of up to 1015 mm or more.
- ❖ The ratios of silicon to chromium and inoculation with ferrosilicon are carefully controlled to control the amount and distribution of the graphite particles.
- ❖ The rolls can be double poured with a gray iron core.
- ❖ With molybdenum modification, the matrix of the chill-cast shell becomes martensitic.
- ❖ Some roll alloys are designed to undergo a modified normalizing heat treatment in order to obtain a bainitic microstructure.

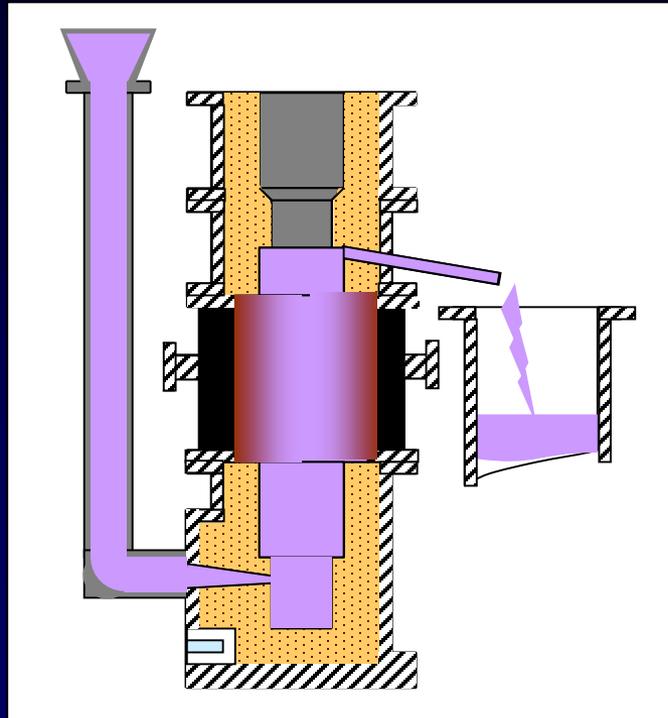


Microstructure of indefinite chill rolls

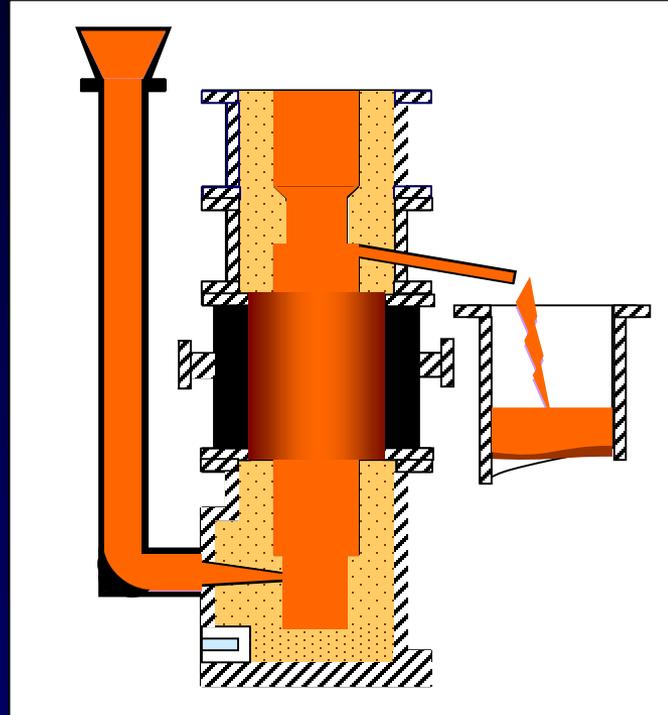
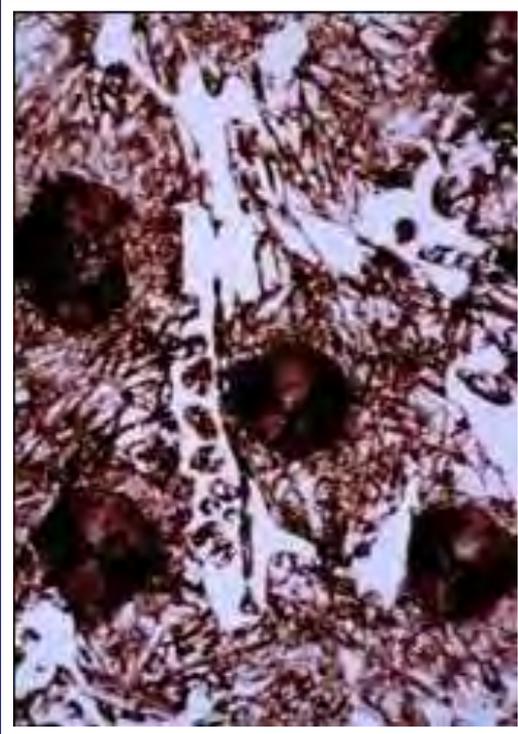
SINGLE Poured ROLLS

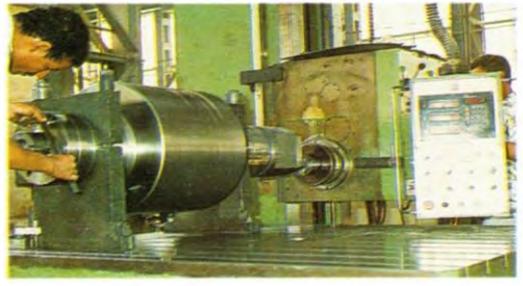


DOUBLE POURED (COMPOSITE) ROLLS



DOUBLE POURED (COMPOSITE) ROLLS





CLASSES OF HIGH-Cr IRONS

Irons for Abrasion Resistance

- ❖ The chromium-molybdenum irons (class II of ASTM A532) contain 11 to 23% Cr and up to 3.5% Mo and can be supplied either as-cast with an austenitic or austenitic-martensitic matrix, or heat treated with a martensitic matrix microstructure for maximum abrasion resistance and toughness.
- ❖ They are usually considered the hardest of all grades of white cast irons.
- ❖ Compared to the lower-alloy nickel-chromium white irons, the eutectic carbides are harder and can be heat treated to achieve castings of higher hardness.
- ❖ Molybdenum, as well as nickel and copper when needed, is added to prevent pearlite and to ensure maximum hardness.

Class	Type	Designation	Composition, wt %								
			C	Mn	Si	Ni	Cr	Mo	Cu	P	S
I	A	Ni-Cr-HiC	2.8-3.6	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	...	0.3 max	0.15 max
I	B	Ni-Cr-LoC	2.4-3.0	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	...	0.3 max	0.15 max
I	C	Ni-Cr-GB	2.5-3.7	2.0 max	0.8 max	4.0 max	1.0-2.5	1.0 max	...	0.3 max	0.15 max
I	D	Ni-HiCr	2.5-3.6	2.0 max	2.0 max	4.5-7.0	7.0-11.0	1.5 max	...	0.10 max	0.15 max

Class	Type	Designation	Hardness value														
			Sand cast, min(a)			Hardened or hardened and stress relieved						Chill cast, min(b)			Softened, max		
			As-cast or As-cast and stress relieved			Level 1			Level 2								
			HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV
I	A	Ni-Cr-HiC	550	53	600	600	56	660	650	59	715	600	56	660
I	B	Ni-Cr-LoC	550	53	600	600	56	660	650	59	715	600	56	660
I	C	Ni-Cr-GB	550	53	600	600	56	660	650	59	715	600	56	660	400	41	430
I	D	Ni-HiCr	500	50	540	600	56	660	650	59	715	550	53	600

- ❖ The high-chromium irons (class III of ASTM A532). These general-purpose irons, also called 25% Cr and 28% Cr irons, contain 23 to 28% Cr with up to 1.5% Mo.
- ❖ To prevent pearlite and attain maximum hardness, molybdenum is added in all but the lightest-cast sections.
- ❖ Alloying with nickel and copper up to 1% is also practiced.
- ❖ Although the maximum attainable hardness is not as high as in the class II chromium-molybdenum white irons, these alloys are selected when resistance to corrosion is also desired.

Class	Type	Designation	Composition, wt %								
			C	Mn	Si	Ni	Cr	Mo	Cu	P	S
III	A	25% Cr	2.0-3.3	2.0 max	1.5 max	2.5 max	23.0-30.0	3.0 max	1.2 max	0.10 max	0.06 max

Class	Type	Designation	Hardness value																	
			Sand cast, min(a)			Hardened or hardened and stress relieved									Chill cast, min(b)			Softened, max		
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			HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV			
III	A	25% Cr	450	46	485	600	56	660	650	59	715	400	41	430			

- ❖ Class I and II high-chromium white irons are superior in abrasion resistance and are used effectively in impellers and volutes in slurry pumps, classifier wear shoes, brick molds, impeller blades and liners for shot blasting equipment, and refiner disks in pulp refiners.
- ❖ In many applications they withstand heavy impact loading, such as from impact hammers, roller segments and ring segments in coal grinding mills, feed-end lifter bars and mill liners in ball mills for hard-rock mining, pulverizer rolls, and rolling mill rolls.

Class	Type	Designation	Composition, wt %								
			C	Mn	Si	Ni	Cr	Mo	Cu	P	S
I	A	Ni-Cr-HiC	2.8-3.6	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	...	0.3 max	0.15 max
I	B	Ni-Cr-LoC	2.4-3.0	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	...	0.3 max	0.15 max
I	C	Ni-Cr-GB	2.5-3.7	2.0 max	0.8 max	4.0 max	1.0-2.5	1.0 max	...	0.3 max	0.15 max
I	D	Ni-HiCr	2.5-3.6	2.0 max	2.0 max	4.5-7.0	7.0-11.0	1.5 max	...	0.10 max	0.15 max
II	A	12% Cr	2.0-3.3	2.0 max	1.5 max	2.5 max	11.0-14.0	3.0 max	1.2 max	0.10 max	0.06 max
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II	D	20% Cr-Mo	2.0-3.3	2.0 max	1.0-2.2	2.5 max	18.0-23.0	3.0 max	1.2 max	0.10 max	0.06 max

Class	Type	Designation	Hardness value																	
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			HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV	HB	HRC	HV			
I	A	Ni-Cr-HiC	550	53	600	600	56	660	650	59	715	600	56	660			
I	B	Ni-Cr-LoC	550	53	600	600	56	660	650	59	715	600	56	660			
I	C	Ni-Cr-GB	550	53	600	600	56	660	650	59	715	600	56	660	400	41	430			
I	D	Ni-HiCr	500	50	540	600	56	660	650	59	715	550	53	600			
II	A	12% Cr	550	53	600	600	56	660	650	59	715	550	53	600	400	41	430			
II	B	15% Cr-Mo	450	46	485	600	56	660	650	59	715	400	41	430			
II	D	20% Cr-Mo	450	46	485	600	56	660	650	59	715	400	41	430			

Examples of High Cr Cast Iron for Abrasion Resistance Castings



Impeller



Volutes



Blades



Impact Hammer



Liners of shot blast machine



Pulp Refiner

Irons for Corrosion Resistance

- ❖ Alloys with improved resistance to corrosion, for applications such as pumps for handling fly ash, are produced with high-chromium content (26 to 28% Cr) and low carbon content (1.6 to 2.0% Cr).
- ❖ These irons provide the maximum chromium content in the matrix.
- ❖ The addition of 2% Mo is recommended for improving resistance to chloride-containing environments.
- ❖ Fully austenitic matrix structures provide the best resistance to corrosion, but some reduction in abrasion resistance must be expected.
- ❖ Castings are normally supplied in the as-cast condition.



Irons for High-Temperature Service

- ❖ **Because of castability and cost, high-chromium white iron castings can often be used for complex and intricate parts in high-temperature applications at considerable savings compared to stainless steel.**
- ❖ **These cast iron grades are alloyed with 12 to 39% Cr at temperatures up to 1040°C for scaling resistance.**
- ❖ **Chromium causes the formation of an adherent, complex, chromium-rich oxide film at high temperatures.**

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- ❖ The high-chromium irons designated for use at elevated temperatures fall into one of three categories, depending on the matrix structure:
 - ❖ Martensitic irons alloyed with 12 to 28% Cr
 - ❖ Ferritic irons alloyed with 30 to 34% Cr
 - ❖ Austenitic irons that contain 15 to 30% Cr as well as 10 to 15% Ni to stabilize the austenite phase.
 - ❖ The carbon content of these alloys ranges from 1 to 2%. The choice of an exact composition is critical to the prevention of σ -phase formation at intermediate temperatures and at the same time avoids the ferrite-to-austenite transformation during thermal cycling, which leads to distortion and cracking.
 - ❖ Typical applications include recuperator tubes; breaker bars and trays in sinter furnaces; grates, burner nozzles, and other furnace parts; glass bottle molds; and valve seats for combustion engines.

Examples of High Cr Cast Iron for High Temp. Resistance Castings



Glass Bottle Molds



Grates



Burner Nozzles



Valve Seats

MICROSTRUCTURES OF HIGH-Cr IRONS

Optimum Metallic Matrix

- ❖ To a large extent, the metal matrix in high-chromium irons has characteristics of tool steel. It can be made tough to increase the tolerance to impact loading, or it can be hardened to reduce wear, although generally at the expense of toughness.
- ❖ Matrix structures can be pearlite, austenite, martensite, or some combination of these.

Pearlitic Matrix Structures:

- ❖ have modest abrasion resistance and low toughness.
- ❖ will occur when hardenability alloying elements are insufficient
- ❖ most of Cr is tied up in Cr-carbides, so other alloying elements are needed to provide adequate hardenability.



Fully Martensitic Matrix

- ❖ Provides maximum abrasion resistance
- ❖ when tempered to minimize retained austenite, provides maximum resistance to spalling and conditions of repeated impact

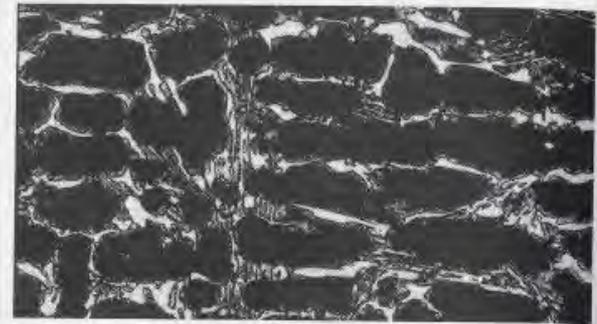
As-cast Austenitic Irons

- ❖ Although relatively soft, can give satisfactory abrasive wear performance, due to pronounced work hardening in service.

Carbides

- ❖ The carbides in high-chromium iron are very hard and wear resistant but are also brittle. In general, wear resistance is improved by increasing the amount of carbide (increasing the carbon content), while toughness is improved by increasing the proportion of metallic matrix (reducing the carbon content).
- ❖ Large hexagonal carbide rods occur when carbon contents exceed the eutectic carbon content.
- ❖ These primary chromium carbides, which precipitate from the melt ahead of eutectic solidification, are quite deleterious to impact toughness and should be avoided in castings subjected to any impact in service.

Microstructures of high-chromium white iron compositions. (a) Low-carbon (hypoeutectic), (b) Eutectic. (c) High-carbon (hypereutectic).



(a)



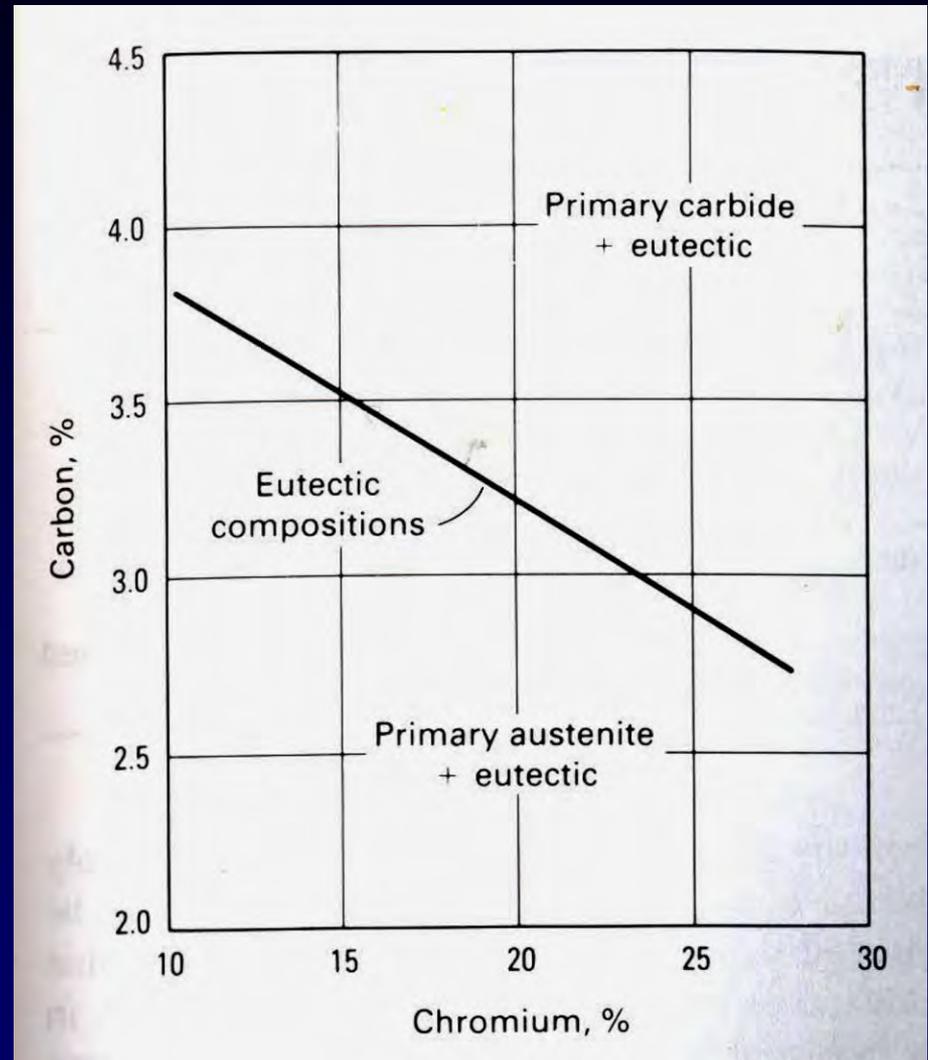
(b)



(c)

- ❖ The eutectic carbon content varies inversely with chromium content in these alloys.

Relationship between the chromium and carbon contents and the eutectic composition in high-chromium white irons.



Grinding Media for Cement & Mineral Processing Industries

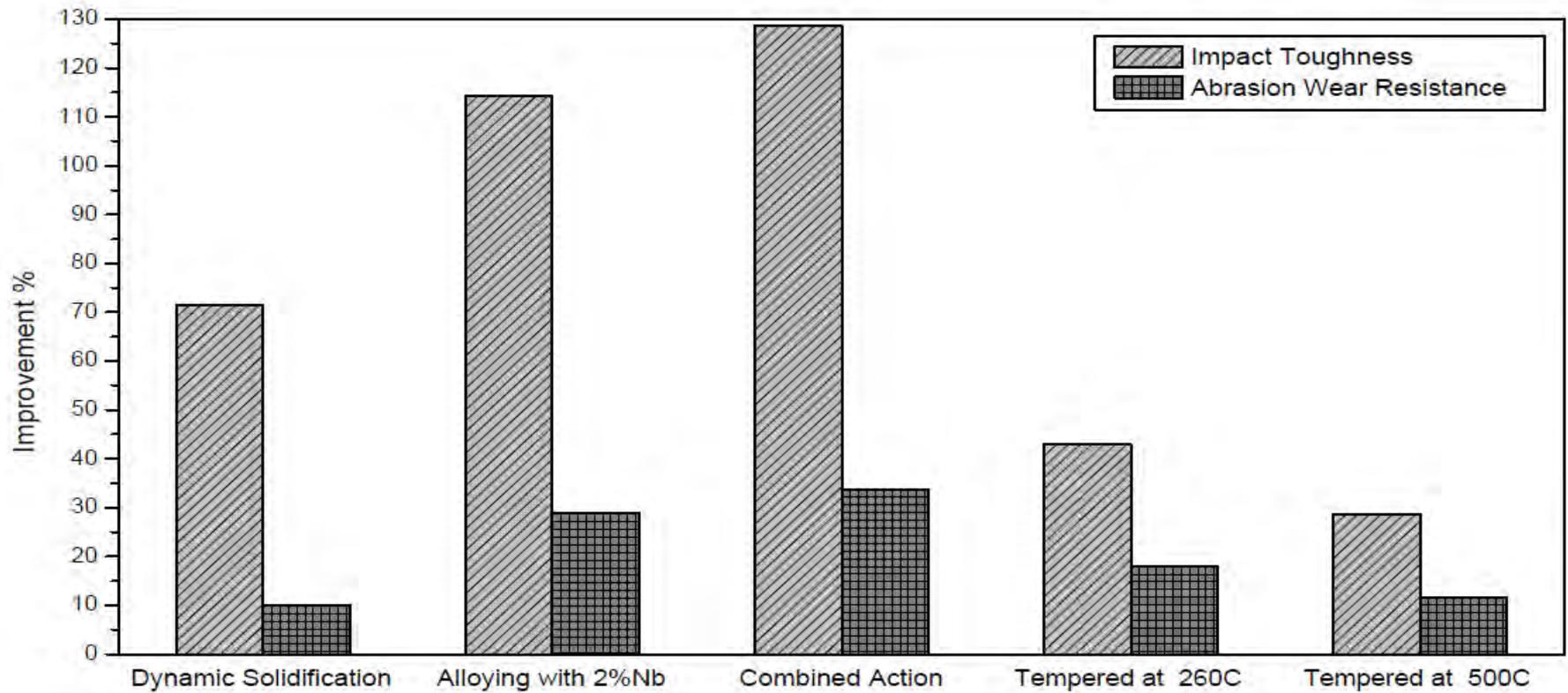
- ❖ High Cr-Mo irons are used in different applications with varying demands for abrasion resistance and fracture toughness.
- ❖ Optimum combination between the two properties was the target of recent research work at CMRDI.





Microstructure of 15%Cr-2%Mo hypereutectic iron: (a) statically solidified and (b) dynamically solidified iron

Optimum combination of properties is always related to structural refinement



The effects of developed practices on improvement the combination between impact toughness and abrasion resistance of 15%Cr-2%Mo hypereutectic iron.

As-Cast Austenitic Microstructures

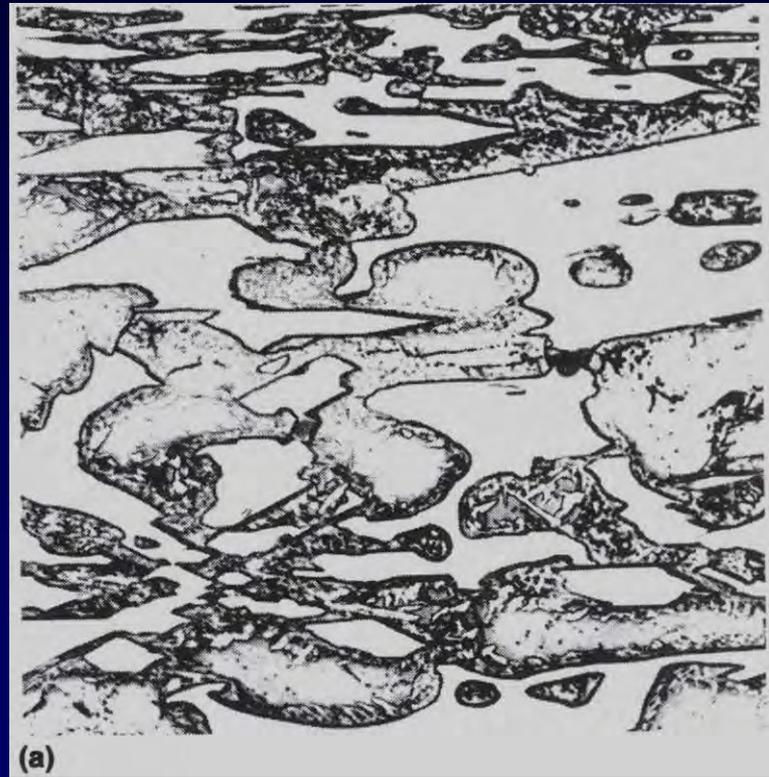
- ❖ Solidification in the hypoeutectic alloys occurs by the formation of austenite dendrites, followed by the eutectic formation of austenite and M_7C_3 chromium carbides.
 - ❖ Under equilibrium conditions, additional chromium carbide precipitates from the austenite matrix on cooling from the eutectic to the critical temperature, about 760°C and transformation to ferrite and carbide occurs on subsequent cooling.
 - ❖ When cooling under nonequilibrium conditions, such as those encountered in most commercial castings, the austenite becomes supersaturated in carbon and chromium.
 - ❖ Due to elevated carbon and chromium contents, a metastable austenitic cast iron normally develops, provided that pearlitic and bainitic transformations have been inhibited.
- ❖ With sufficient alloying with molybdenum, manganese, nickel, and copper, pearlitic transformation can be avoided in virtually any cast section.



High-chromium white iron with an as-cast austenitic matrix microstructure.

As-Cast Martensitic Microstructures

- ❖ Martensitic structures can be obtained as-cast in heavy-section castings that cool slowly in the mold. With slow cooling rates, austenite stabilization is incomplete and partial transformation to martensite occurs.
- ❖ In these castings martensite is mixed with large amounts of retained austenite, and therefore hardness levels are lower than can be achieved in heat-treated martensitic castings.
- ❖ These castings must contain sufficient alloy to suppress pearlite on cooling.



Heat-Treated Martensitic Microstructures

- ❖ Some compositions with higher silicon contents have been developed to assist martensite formation in refrigeration treatments.
- ❖ Subcritical annealing has been employed to reduce austenite content and increase hardness and toughness.
- ❖ To obtain maximum hardness and abrasion resistance, martensitic matrix structures must be produced by full heat treatment. The casting must contain sufficient alloy to avoid pearlite formation on cooling from the heat treatment temperature.



High-chromium iron microstructures. (a) As-cast austenitic martensitic matrix microstructure. (b) Heat-treated martensitic microstructure.

As-Cast Pearlitic Microstructures

- ❖ For castings that will be heat treated, the desired mold-cooled structure is often pearlite. This softer structure will facilitate removal of gates and risers and minimize the transformational and thermal stresses that cause cracking.
- ❖ The pearlitic structure will also shorten the response to heat treatment.
- ❖ Careful design of alloy composition will ensure that a substantially pearlitic structure develops in the casting after mold cooling, but will provide enough hardenability to prevent pearlite formation during subsequent heat treatment.
- ❖ Heavy-section castings made pearlitic by such an alloy content can oftentimes be removed from the mold once the castings have reached black heat.

Selecting Compositions to Obtain Desired Structures

- ❖ Many complex sections, such as slurry pump components, are used in the as-cast austenitic/martensitic condition to avoid the possibility of cracking and distortion when heat treated.
- ❖ To prevent pearlite in mold cooling, alloying additions are usually required. As the carbon content is increased, more chromium is consumed, so that additional carbide forms and larger alloying additions are required.

Minimum alloy content to avoid pearlite in mold-cooled castings for indicated effective section size (plate thickness or radius of rounds)

ASTM A 532 class	Cr(a), %	C(a), %	Plate thickness or radius of rounds		
			25 mm (1 in.)	50 mm (2 in.)	100 mm (4 in.)
IIB, C	14-18	2.0	1.0 Mo	1.5 Mo	1.5 Mo + 1.0 (Ni + Cu)
		3.5	2.0 Mo	2.5 Mo	2.5 Mo + 1.0 (Ni + Cu)
IID, E	18-23	2.0	0.5 Mo	1.0 Mo	1.0 Mo + 1.0 (Ni + Cu)
		3.2	1.5 Mo	2.0 Mo	2.0 Mo + 1.0 (Ni + Cu)
IIIA	23-28	2.0	...	0.5 Mo	1.0 Mo
		3.0	1.0 Mo	1.5 Mo	1.5 Mo + 1.0 (Ni + Cu)

(a) In base irons containing 0.6% Si and 0.8% Mn

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- ❖ **Optimum performance is usually achieved with heat-treated martensitic structures, again, alloying must be sufficient to ensure a pearlite-free microstructure with heat treatment.**
 - ❖ **The heat treatment requires an air quench from the austenitizing temperature. Faster cooling rates should not be used, because the casting can develop cracks due to high thermal and/or stresses.**
 - ❖ **Thus, the alloy must have sufficient hardenability to allow air hardening. However, overalloying with manganese, nickel, and copper promotes retained austenite, which detracts from resistance to abrasion and spalling.**
 - ❖ **Therefore, it is best to obtain adequate hardenability primarily with molybdenum.**

- ❖ A guide to alloying for air quenching heat-treated castings of various sections is given below.

Minimum alloy content to avoid pearlite in heat treatment for indicated effective section size (plate thickness or radius of rounds)

ASTM A 532 class	Cr(a), %	C(a), %	Plate thickness or radius of rounds		
			50 mm (2 in.)	125 mm (5 in.)	150-255 mm (6-10 in.)
IIB, C	14-18	2.0	1.5 Mo	1.5 Mo + 0.5 (Ni + Cu)	2.0 Mo + 1.0 (Ni + Cu)
		3.5	3.0 Mo	2.0 Mo + 1.0 (Ni + Cu)	2.5 Mo + 1.2 (Ni + Cu)(b)
IID, E	18-23	2.0	1.0 Mo	2.0 Mo	2.0 Mo + 0.5 (Ni + Cu)
		3.2	1.5 Mo	2.0 Mo + 0.7 (Ni + Cu)	2.0 Mo + 1.2 (Ni + Cu)(b)
IIIA	23-28	2.0	0.5 Mo	1.5 Mo	1.5 Mo + 0.5 (Ni + Cu)
		3.0	1.5 Mo	1.5 Mo + 0.6 (Ni + Cu)	1.5 Mo + 1.2 (Ni + Cu)(b)

(a) In base irons containing 0.6% Si and 0.8% Mn. (b) Nickel and copper promote retained austenite and should be restricted to combined levels of 1.2% maximum; manganese behaves similarly and should be restricted to 1.0% maximum.

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- ❖ As with steels, maximum abrasion resistance is achieved with a fully martensitic matrix structure.
 - ❖ As-cast austenitic iron, although relatively soft, can give satisfactory performance in many abrasive wear applications due to pronounced work hardening in service.
 - ❖ Resistance to crack propagation is greatest in irons having a fully austenitic matrix.
 - ❖ Under conditions of repeated impact, martensitic irons, which have been tempered to minimize retained austenite, have the maximum resistance to spalling.
 - ❖ Pearlitic, matrix structures have modest abrasion resistance and low toughness, and therefore they are not generally desirable.
 - ❖ Pearlite will always occur when alloying is insufficient to inhibit its formation.

- ❖ Most of the chromium is tied up in the chromium carbides, so other alloying relatively low-cost material will have adequate wear resistance, higher-cost material will have measurably superior wear resistance.
- ❖ The ratio of wear rate to replacement cost should be evaluated. This ratio can be an effective means of evaluating the most economical use of materials.

❖ It is often more economical to use a less wear-resistant material and replace it more often.

HOWEVER

❖ In some cases, such as when frequent occurrences of downtime cannot be tolerated, economy is less important than service life.

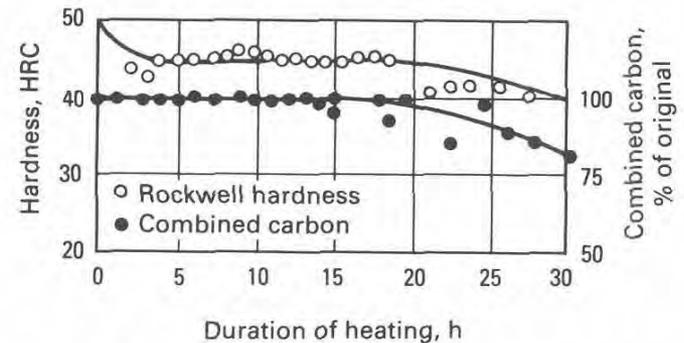
CALCULATIONS OF COST EFFECTIVENESS MUST TAKE INTO ACCOUNT

- ❖ The actual cost of materials
- ❖ Cost of heat treatment
- ❖ Time for removal of worn parts and insertion of new parts
- ❖ Other production time lost

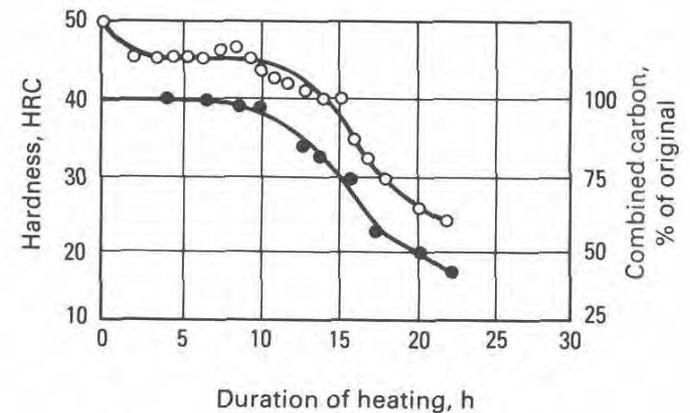
HEAT TREATMENT

i) For unalloyed or low-Cr pearlitic white irons

- ❖ Heat treatment is performed primarily to relieve the internal stresses that develop in the castings as they cool in their molds. Generally, such heat treatments are used only on large castings such as mill rolls and chilled iron car wheels.
- ❖ Temperatures up to about 705°C can be used without severely reducing abrasion resistance. In some cases, the castings can be removed from their molds above the pearlitic-formation temperature and can then be isothermally transformed to pearlite (or to ferrite and carbide) in an annealing furnace.



(a)

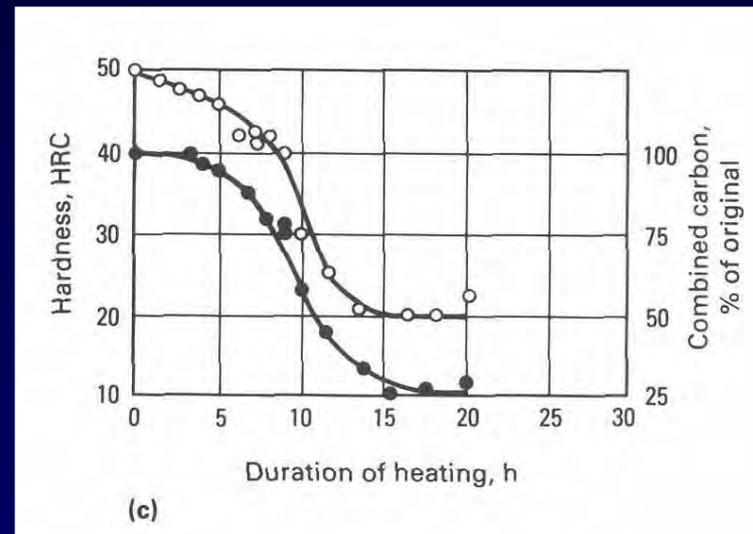


(b)

i) For unalloyed or low-Cr pearlitic white irons (Cont'd.)

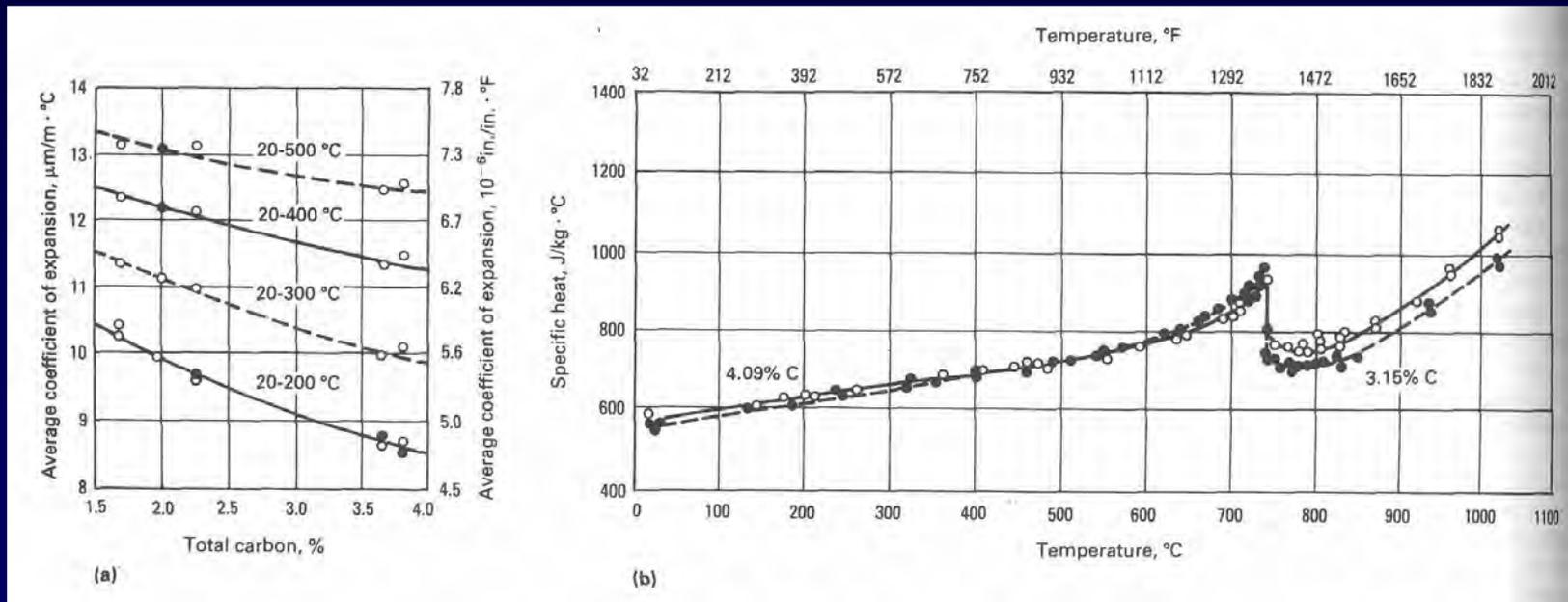
- ❖ As the tempering or annealing temperature is increased, the time at temperature must be reduced to prevent graphitization.

3.60% C, 0.5-0.55% Si, 0.60% Mn, 0.33% P, 0.13% S



Effect of annealing on hardness and combined carbon content in chilled iron. Effect of heating at (a) 815 °C, (b) 845 °C, or (c) 870 °C on hardness and combined carbon content of chilled portion of a chilled iron casting.

- ❖ Residual stresses in large castings result from volume changes during the transformation of austenite and during subsequent cooling of the casting to room temperature.
- ❖ Because these volume changes may not occur simultaneously in each part of the casting, they tend to set up residual stresses, which may be very high and may therefore cause the casting to crack in the foundry or in service.



Thermal expansion (a) and specific heat (b) of white iron.

ii) The nickel-chromium martensitic white irons

- ❖ The nickel-chromium martensitic white irons, containing up to about 7% Ni and 11% Cr, usually put into service after only a low-temperature heat treatment at 230 to 290°C to temper the martensite and to increase toughness.
- ❖ If retained austenite is present and the iron therefore has less than optimum hardness, a subzero treatment down to liquid nitrogen temperature can be employed to transform much of the retained austenite to martensite.
- ❖ Subzero treatment substantially raises the hardness, often as much as 100 Brinell points.
- ❖ Following subzero treatment, the castings are almost always tempered at 230 to 260°C.
- ❖ The austenite-martensite-martensite microstructures produced in nickel-alloyed irons are often, desirable for their intrinsic toughness.
- ❖ It is possible to transform additional retained austenite by heat treating nickel-chromium white irons at about 730°C. Such treatment decreases matrix carbon and therefore raises the M_s temperature.
- ❖ However, high-temperature treatments are usually less desirable than subzero treatments, because the former are more costly and more likely to induce cracking due to transformation stresses.

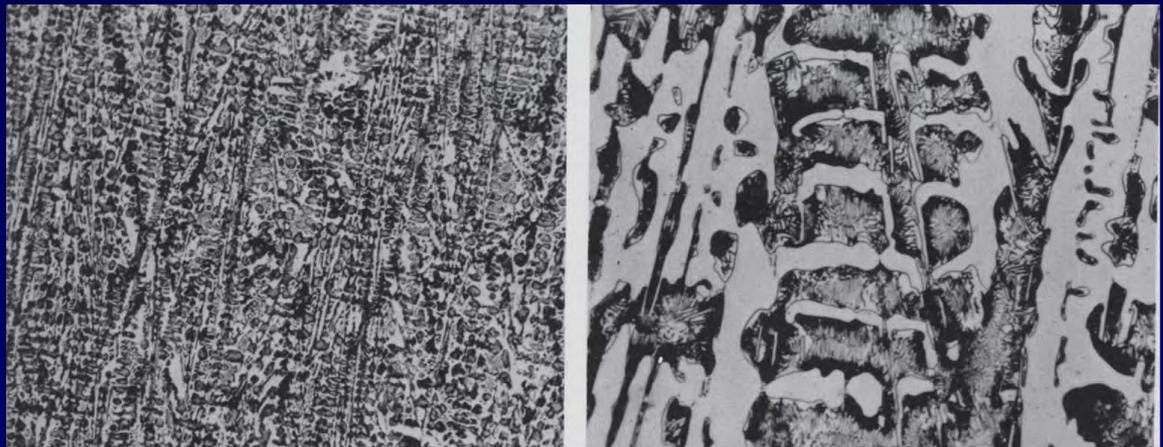
iii) The high-chromium martensitic white irons (>12% Cr)

- ❖ The high-chromium martensitic white irons (>12% Cr) must be subjected to a high-temperature heat treatment to develop full hardness. They can be annealed to soften them for machining, then hardened to develop the required abrasion resistance.
- ❖ Because of their high chromium content, there is no likelihood of graphitization while the castings are held at the re-austenitizing temperature.
- ❖ The usual re-austenitizing temperature for high-temperature irons ranges from about 950°C for a 15Cr-Mo iron to about 1065°C for a 27% Cr iron.
- ❖ An appreciable holding time (3 to 4 h minimum) at temperature is usually mandatory to permit precipitation of dispersed secondary carbide particles in the austenite.
- ❖ This lowers the amount of carbon dissolved in the austenite to a level that permits transformation to martensite during cooling to room temperature.
- ❖ Air quenching is usually used, although small, simply shaped castings can be quenched in oil or molten salt without producing quench cracks.
- ❖ Following quenching, it is advisable to stress relieve (temper) the castings at about 200°C.

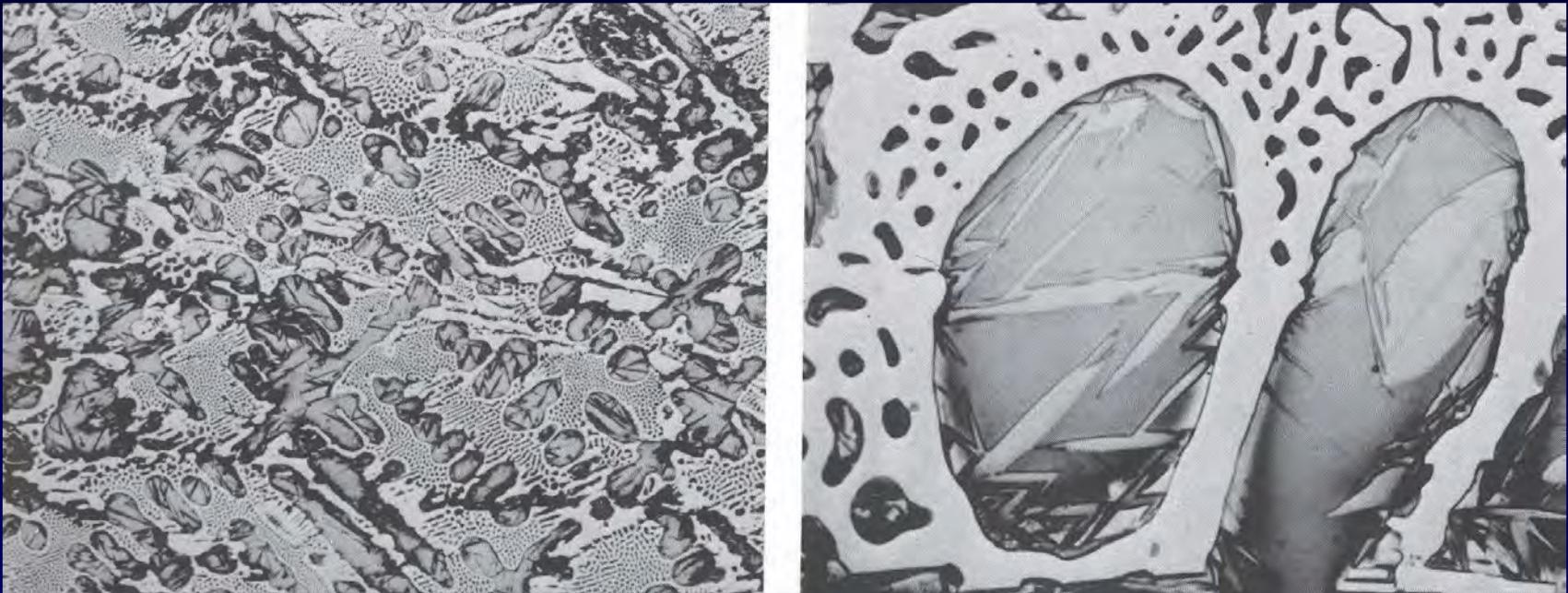
EFFECT OF PROCESSING ON MICROSTRUCTURE

- ❖ With rapid solidification, such as that which occurs in thin-wall castings or when the iron solidifies against a chill, the austenite dendrites and eutectic carbides are fine grained, which tends to increase fracture toughness.
- ❖ In low-chromium white irons, rapid solidification will also reduce any tendency toward formation of graphite. The presence of graphite severely degrades abrasion resistance.
- ❖ Chills in the mold can be used to promote directional solidification and therefore reduce shrinkage cavities in the casting.
- ❖ Certain inoculants, notably bismuth, may beneficially alter the solidification pattern by reducing spiking or by producing a finer as-cast grain size.

*Structure of unalloyed chill-cast iron.
Composition: 3.6TC-0.7Si-0.8Mn.
Structure shows coarse lamellar
pearlite and ferrite in a matrix of
 M_3C carbides.*

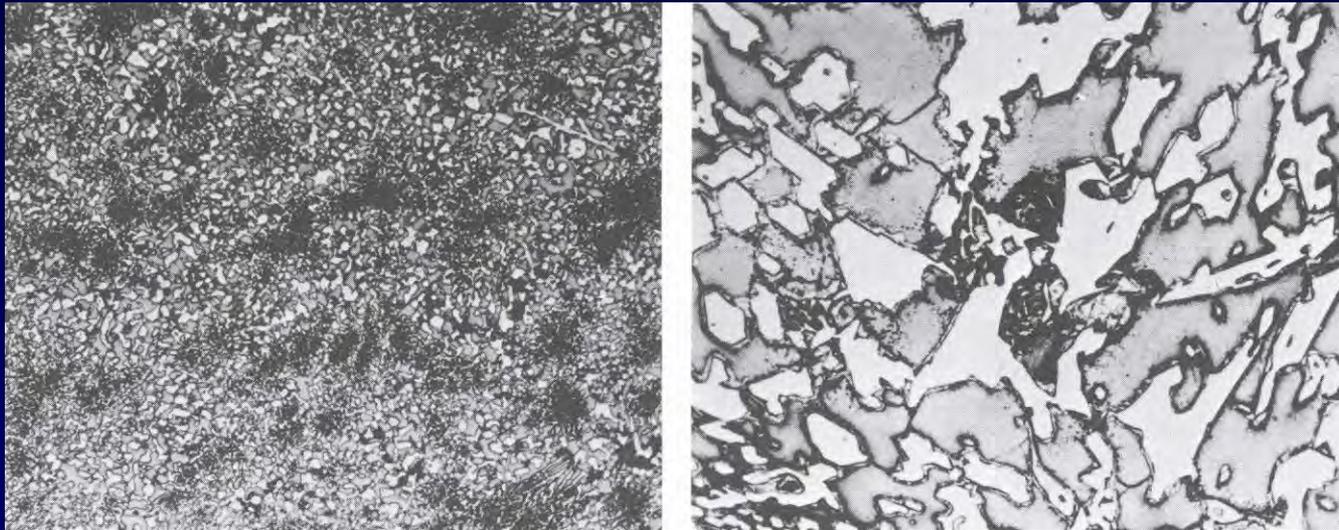


- ❖ Immediately after solidification, the microstructure of unalloyed or iron-chromium white irons consists of austenite dendrites, containing up to about 2% C, surrounded by M_3C carbides.



Structure of sand-cast white iron. Composition: 3.4%C-0.4Si-0.6Mn-1.4Cr-3.0Ni. Structure shows austenite-martensite in a matrix of M_3C carbides.

- ❖ When the chromium content of the iron exceeds about 7 wt%, the structure contains M_7C_3 eutectic carbides surrounded by austenite.
- ❖ This reversal of the continuous phase in the structure tends to increase the fracture toughness of white irons, but only those irons that have a hypoeutectic or eutectic carbon equivalent.
- ❖ All hypereutectic white irons are relatively brittle and are seldom used commercially.



Structure of sand-cast white iron. Composition: 3.5TC-0.4Si-0.8Mn-16.0Cr-3.0Ni. Structure shows M_7C_3 carbides in a matrix of austenite containing small amounts of pearlite and martensite.

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- ❖ **After a white iron casting has solidified and begins to cool to room temperature, the carbide phase may decompose into graphite plus ferrite or austenite.**
 - ❖ **This tendency to form graphite can be suppressed by rapid cooling or by the addition of carbide-stabilizing alloying elements (usually chromium, although inoculating with tellurium or bismuth is also effective).**
 - ❖ **Austenite in the solidified white iron structure normally undergoes several changes as it cools to ambient temperature:**
 - i) If it is cooled slowly enough, it tends to reject hypereutectoid carbon, either on existing eutectic carbide particles or as particles, platelets, or spines within the austenite grains. This precipitation occurs principally between about 1050 and 750°C. The rate precipitation depends on both time and temperature.**
 - ii) As the austenite cools further, through the range of 700 to 540°C, it tends to transform to pearlite. This transformation can be suppressed, however, by rapid cooling and/or by the use of pearlite-suppressing elements in the iron.**



Nickel, manganese, and copper are the principal pearlite-suppressing elements.

Chromium does not contribute significantly to pearlitic suppression (hardenability) in many white irons, because most of the chromium is tied up in carbides.

Molybdenum, a potent carbides former, is also tied up in carbides, but in high-chromium irons, enough chromium and molybdenum remain in the matrix to contribute significantly to hardenability.

- iii) Upon cooling to below about 540°C, the austenite may transform to bainite or martensite, thus producing martensitic white iron, which is currently the most widely used type of abrasion-resistant white iron.**

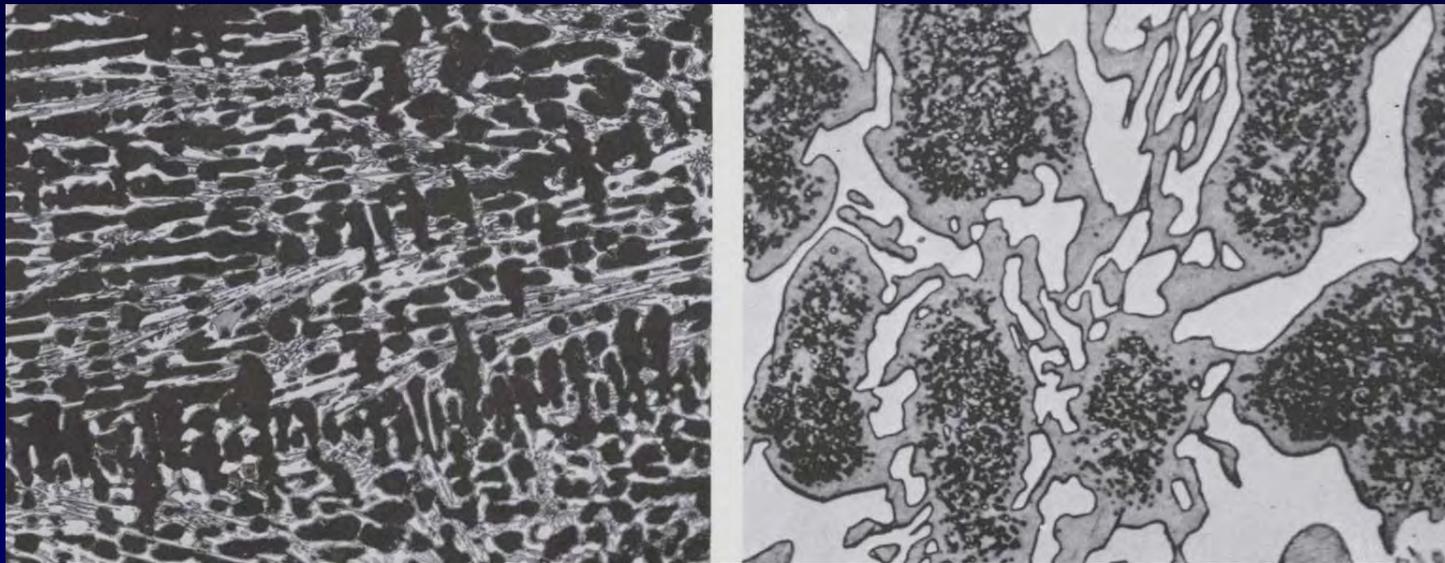
Martensitic white irons usually contain some retained austenite, which is not considered objectionable unless it exceeds about 15%.

Retained austenite is metastable and may transform to martensite when plastically deformed at the wearing surface of the casting.

Effect of Silicon on Microstructure

- ❖ Silicon has a substantial influence on the microstructure of any grade of white iron. Normally, the silicon content exceeds 0.3%, and it may range as high as 2.2% in some of the high-chromium grades.
- ❖ During the solidification of unalloyed or low-alloy irons, silicon tends to promote the formation of graphite, an effect that can be suppressed by rapid solidification or the addition of carbide-stabilizing elements.
- ❖ After solidification, either while the casting is cooling to ambient temperature or during subsequent heat treatment, silicon tends to promote the formation of pearlite in the structure, but only if it is the only alloy present.
- ❖ In the presence of chromium and molybdenum, both of which suppress ferrite, silicon has a minimal effect on ferrite and substantially suppresses bainite.

- ❖ In certain alloy white irons with high retained-austenite contents, increasing the silicon content raises the M_s temperature of the austenite, which in turn promotes the transformation of austenite to martensite.
- ❖ Silicon is also used to enhance the hardening response when the castings are cooled below ambient temperature.



Structure developed by the heat treatment of a high-chromium iron. Specimen from a chute liner 50 mm thick, containing 2.6% total carbon, 1.5% Si, 1.1% Mn, 14.3% Cr, and 3.0% Mo, reheated to 1040 to 1065 °C and air cooled. Structure is M_7C_3 eutectic carbides in a matrix of martensite and fine spheroidized M_3C carbides.

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- ❖ **Hardness is the principal property of white iron that is routinely determined and reported. Other (nonstandard) tests to determine strength, impact resistance, and fracture toughness are sometimes employed by individual users, producers, or laboratories. Because of the difficulty of preparing test specimens, especially from heavy-section castings, these nonstandard tests are seldom used for routine quality control.**
 - ❖ **Two exceptions are the tumbling-breakage test and the ball-on-ball impact spalling test, which have been routinely used by certain producers for testing grinding balls.**
 - ❖ **Minimum hardness values for pearlitic white irons are 321 HB for the low-carbon grade and 400 HB for the high-carbon grade. A chill-cast high-carbon 2% Cr white iron may reach a hardness of about 600 HB.**
 - ❖ **A typical hardness range for a sand-cast high-carbon grade is about 450 to 550 HB.**

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- ❖ **The minimum hardness specified for the hardened (heat-treated) class II castings is well below the average expected hardness.**
 - ❖ **These irons, when fully hardened so that they are free from high-temperature products of austenite transformation, will have hardness values ranging from about 800 to 950 HV (depending on retained austenite content). The 800 to 950 HV range is equivalent to 700 to 790 HB or 62.5 to 67.5 HRC.**
 - ❖ **For optimum abrasion resistance of the class I irons in Table 1, the minimum Brinell hardness, as measured with a tungsten carbide ball or converted from HV or HRC values, should be 700 HB.**

❖ Hardness conversions for white irons are somewhat different from the published data for steel. The next table lists data for two classes of white irons: high-chromium irons and nickel-chromium irons. Because of inherent variations in structure for many cast irons, hardness conversion must be made cautiously. For example, Brinell hardness tests are more consistent and reliable for coarse structures such as those typical of heavy sections.

❖ The hardness ranges that can be expected in high-Cr irons with different microstructures in abrasion resistant irons.

Typical hardness range for the matrices found in white irons

Matrix structure	Hardness, HB
Pearlite	320-500
Austenite	420-500
Martensite (as-cast)	550-650
Martensite (heat treated)	650-850

Hardness conversions for white cast irons (from averaged data)

HB	HV	HRC	Scleroscope
High-chromium irons			
815	1000	68.5	...
800	975	68	...
790	950	67.5	...
775	925	67	...
760	900	66	...
745	875	65.0	...
730	850	64.5	...
720	825	63.5	...
700	800	62.5	...
680	775	61.5	...
660	750	61.0	...
640	725	59.5	...
625	700	58	...
610	675	57	...
585	650	56	...
560	625	54.5	...
540	600	53	...
520	575	51.5	...
490	550	50	...
475	525	48.5	...
440	500	47	...
420	475	45.5	...
395	450	43.5	...
370	425	41.7	...
...	400	40	...
Nickel-chromium irons			
750	830-860	...	90-93
700	740-770	...	84-87
650	690-720	...	79-82
600	630-660	...	75-78
550	570-610	...	70-73
500	510-540	...	67-70

- ❖ The hardness values of microconstituents in abrasion-resistant irons, as well as the hardness of minerals being crushed. It is evident that carbides and martensite are needed to resist abrasion by the common minerals associated with mining and oil drilling.

Hardness of minerals and microconstituents

Mineral	Hardness		Material or microconstituents	Hardness	
	Knoop	HV		Knoop(a)	HV
Talc	20	...	Ferrite	235	70-200
Carbon	35	...	Pearlite, unalloyed	...	250-320
Gypsum	40	36	Pearlite, alloyed	...	300-460
Calcite	130	140	Austenite, 12% Mn	305	170-230
Fluorite	175	190	Austenite, low alloy	...	250-350
Apatite	335	540	Austenite, high-Cr iron	...	300-600
Glass	455	500	Martensite	500-800	500-1010
Feldspar	550	600-750	Cementite (Fe ₃ C)	1025	840-1100
Magnetite	575	...	Chromium carbide (Fe,Cr) ₇ C ₃	1735	1200-1600
Orthoclase	620	...	Molybdenum carbide (Mo ₂ C)	1800	1500
Flint	820	950	Tungsten carbide (WC)	1800	2400
Quartz	840	900-1280	Vanadium carbide (VC)	2660	2800
Topaz	1330	1430	Titanium carbide (TiC)	2470	3200
Garnet	1360	...	Boron carbide (B ₄ C)	2800	3700
Emery	1400	...			
Corundum (alumina)	2020	1800			
Silicon carbide	2585	2600			
Diamond	7575	10000			

(a) Typical values. Source: Ref 4

R. Gundlach and J.L. Parks, Influence of Abrasive Hardness on Wear Resistance of High-Chromium Irons, Wear, Vol 46, 1978, p. 97.

MECHANICAL PROPERTIES

- ❖ Limited data indicate that the yield strengths of white irons are about 90% of their tensile strengths.
- ❖ These data are extremely sensitive to variations in specimen alignment during testing.
- ❖ Because of the near-zero ductility of white irons, the usefulness of tensile test data for design or quality assurance is limited.

Tensile Strength (in reality, the fracture strength)

Pearlitic white irons	from	205 MPa	for high-C grades
	to	415 MPa	for low-C grades

Martensitic white irons

(with M_3C carbides)		from	345-415 MPa
(with M_7C_3 carbides)	from	415-500 MPa	

- ❖ Transverse strength, which is an indirect measurement of tensile strength and tensile ductility, can be determined with a moderate degree of accuracy on unmachined cast test bars.
- ❖ The product of transverse strength and deflection provides one measure of toughness.
- ❖ Values of transverse strength, deflection, and toughness for as-cast test bars should be considered very general; the wide spread of these data emphasizes that properties depend on a marked degree on composition and the conditions under which the castings were produced.

Transverse strengths and relative toughness of various pearlitic and martensitic white irons in the as-cast condition

Data from as-cast 30.5 mm (1.2 in.) diam test bars broken over a 457 mm (18 in.) span

Type of iron	Basic composition	Transverse strength		Deflection		Toughness(a)	
		kg	lb	mm	in.	kg · m	lb · in.
Sand-cast pearlitic	3.2-3.5 C, 1.2 Cr	635-815	1400-1800	2.0-2.3	0.080-0.092	1.29-1.87	112-162
Sand-cast martensitic	2.8-3.6 C, 1.4-4 Cr, 3.3-5 Ni	1810-2490	4000-5500	2.0-3.0	0.08-0.12	3.68-7.60	320-660
	2.5-3.6 C, 7-11 Cr, 4.5-7 Ni	2270-2720	5000-6000	2.0-2.8	0.08-0.11	4.6-7.60	400-660
	2.8-3.4 C, 12-16 Cr, 2-4 Mo	1015-1370	2235-3015	3.2-3.6	0.125-0.14	3.21-4.93	279-422
Chill-cast martensitic	3.5-4.1 C, 12-16 Cr, 2.5-3 Mo	800-1000	1760-2200	2.0-2.8	0.08-0.110	1.60-2.80	140-240
	2.8-3.6 C, 1.4-4 Cr, 3.3-5 Ni	2040-3180	4500-7000	2.0-3.0	0.08-0.12	4.15-9.68	360-840
	2.5-3.6 C, 7-11 Cr, 4.5-7 Ni	2500-3180	5500-7000	2.5-3.8	0.10-0.15	6.34-12.1	550-1050
	3.2-3.4 C, 12-16 Cr, 1.5-3 Mo	1980-2295	4360-5060	5.1-6.5	0.202-0.26	10-15.2	870-1320
	3.5-4.1 C, 12-16 Cr, 2.5-3 Mo	1270-1575	2800-3470	3.6-3.8	0.140-0.15	4.52-6.0	392-520

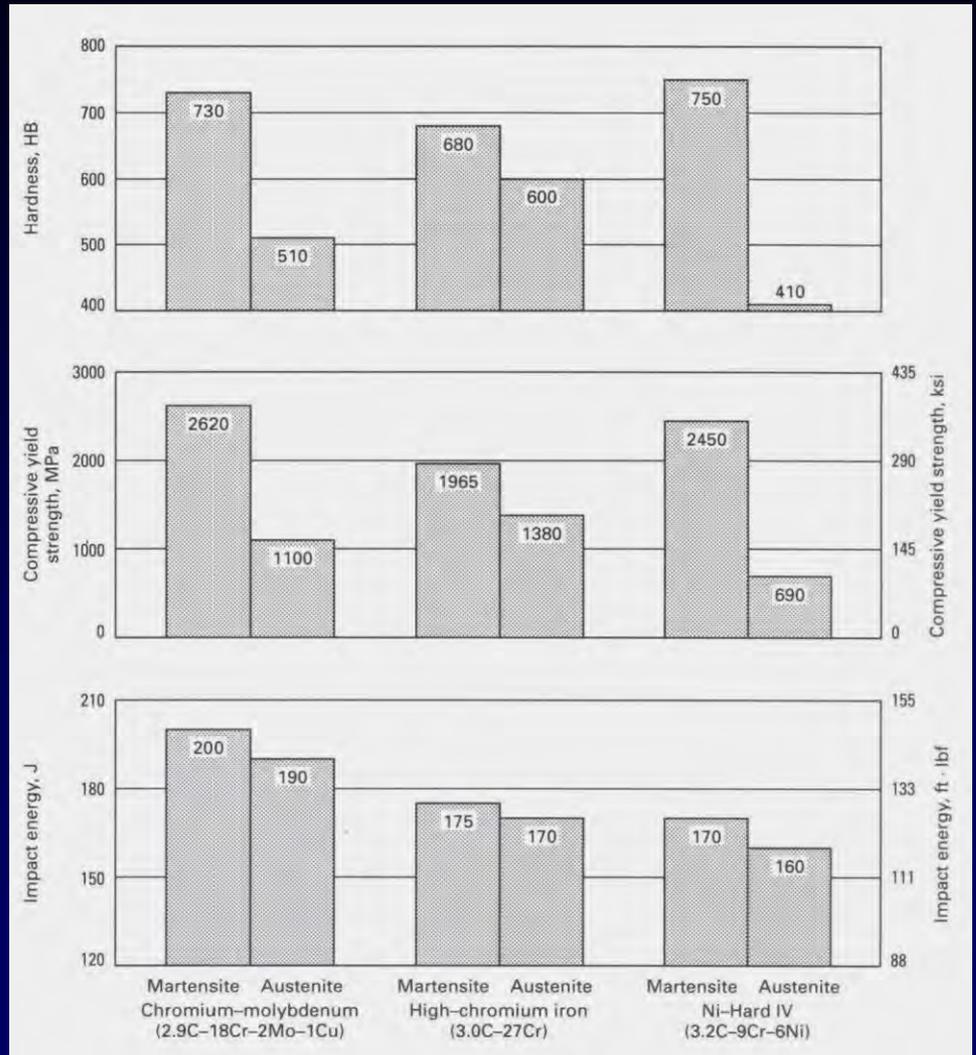
Typical mechanical properties of alloyed white irons

- ❖ Hardness, yield strength in compression, and impact energy absorbed by unnotched Charpy specimens for as-cast austenitic and heat-treated martensitic irons.
- ❖ The chromium-molybdenum iron conforms to ASTM class II type E, the high-chromium iron conforms to ASTM class III type A, and the Ni-Hard IV iron conforms to ASTM class I type D.

The elastic modulus of a white iron

- ❖ The elastic modulus of a white iron is considerably influenced by its carbide structure. An iron with M_3C eutectic carbides has a tensile modulus of 165 to 195 GPa, irrespective of whether it is pearlitic or martensitic, while an iron with M_7C_3 eutectic carbides has a modulus of 205 to 220 GPa.

*“Chrome-Moly White Cast Irons”, Publication
M-630 AMAX, Inc., 1986*



Typical mechanical properties of white cast irons.

OPTIMIZING ABRASION RESISTANCE AND FRACTURE TOUGHNESS

- ❖ Chromium-molybdenum white cast irons are well known for their good abrasion resistance. Abrasion is a type of wear that occurs under the relative movement of a hard body (e.g. mineral or work-hardened wear particle) and the softer surface of a mating material.
- ❖ In the abrasive process, the hard body may be fractured and the softer surface will be cracked and/or deformed, and the material will be removed from the surface, resulting in a measurable volume loss.
- ❖ Mining and earthmoving equipment must withstand severe service stresses and loading rates, so industrial applications of white cast irons under abrasive conditions are frequently limited by their toughness.
- ❖ Generally, abrasion resistance increases with increasing material hardness, while fracture toughness decreases with increasing hardness or strength. Therefore, an opposite effect of hardness on the two properties must be expected.
- ❖ In addition to being influenced by hardness, abrasion resistance depends on microstructural parameters such as quantity of carbides, carbide morphology, retained austenite, internal notches, and the structure of the matrix. These factors also influence fracture toughness.

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- ❖ In order to determine the relationships between hardness, abrasion resistance, and fracture toughness, 13 molybdenum-bearing high-chromium white irons with varying carbide volumes were tested for dynamic fracture toughness (K_{1d}) and wet sand abrasion resistance.
 - ❖ Carbon content was varied from 1.4 to 3.9% and chromium content was varied from 11.6 to 25.7%. Slight variations in copper content were also made. The matrix microstructures that were employed included predominantly austenitic structures and predominantly martensitic structures.
 - ❖ In addition, one composition of white iron (heat No. 63) was subjected to 30 different heat treatments to define the effect of matrix microstructure on dynamic fracture toughness and abrasion resistance. The following figure summarizes these heat treatments.

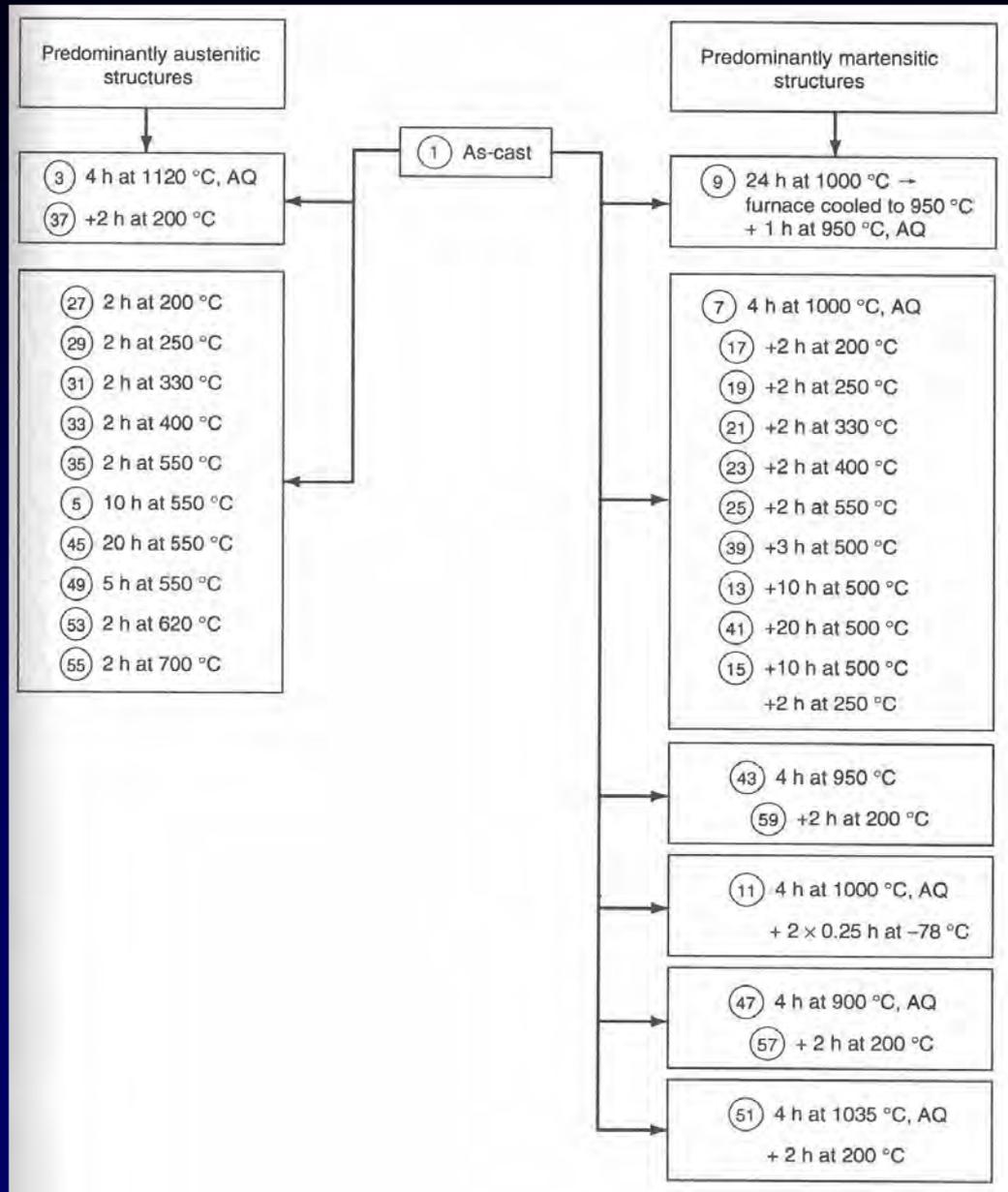
Chemical composition and carbide volume of the high chromium-molybdenum irons tested for dynamic fracture toughness and abrasion resistance

Heat No.	Composition, wt % (a)(b)									Carbide volume, %
	C	Si	Mn	Cr	Mo	Cu	Ni	P	S	
17A	1.41	0.58	1.56	11.6	2.39	1.24	0.020	0.018	0.030	7.1
17B	1.38	(0.58)	(1.56)	12.8	(2.39)	(1.24)	(0.020)	(0.018)	(0.030)	9.8
18A	2.00	0.59	1.54	15.8	2.35	1.14	0.020	NA	NA	14.4
18B	1.89	(0.59)	(1.54)	17.8	(2.35)	(1.14)	(0.020)	NA	NA	17.4
16A	2.58	0.56	1.50	17.6	2.39	1.03	0.023	0.020	0.030	24.3
16B	2.48	(0.56)	(1.50)	18.7	(2.39)	(1.03)	(0.023)	(0.020)	(0.030)	22.7
19A	2.87	0.58	1.52	20.0	2.36	0.94	0.020	NA	NA	29.1
19B	2.79	(0.58)	(1.52)	21.0	(2.36)	(0.94)	(0.020)	NA	NA	30.4
63	2.92	0.57	1.55	19.0	2.35	0.94	0.04	0.032	0.025	28.0
20A	3.50	0.61	1.59	23.4	2.47	0.87	0.022	0.020	0.030	37.6
20B	3.41	(0.61)	(1.59)	24.1	(2.47)	(0.87)	(0.022)	(0.020)	(0.030)	41.1
21A	3.93	0.63	1.57	24.6	2.45	0.76	0.022	NA	NA	45.4
21B	3.81	(0.63)	(1.57)	25.7	(2.45)	(0.76)	(0.022)	NA	NA	38.8

(a) Values in parentheses were not analyzed but are assumed to be the same as those obtained in the "A" casting from the same heat. (b) Not analyzed (NA). Source: Ref 6

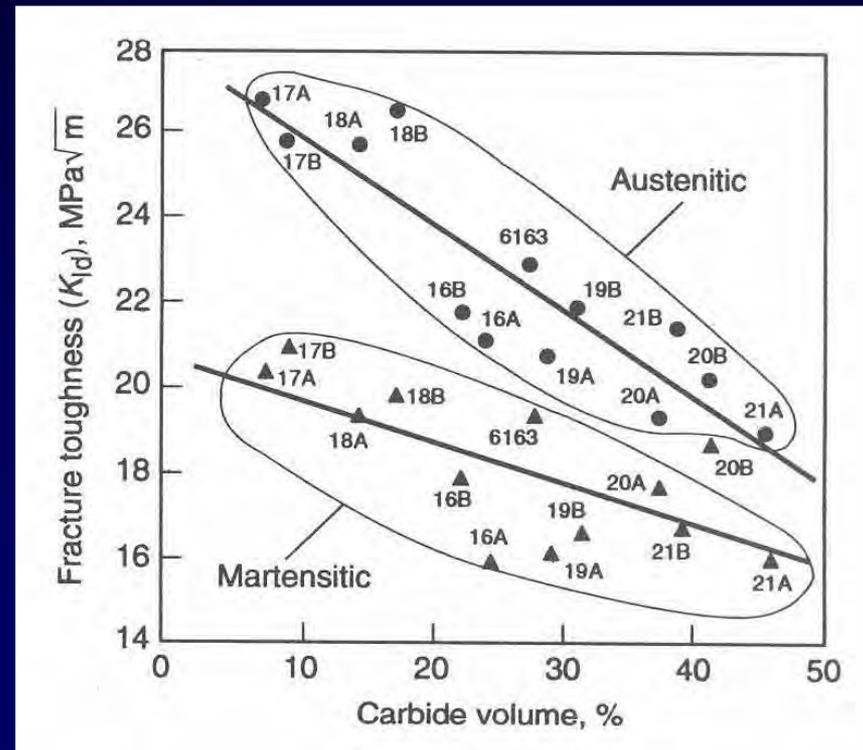
K.-H. Zum Gahr and D.V. Doane, Optimizing Fracture Toughness and Abrasion Resistance in White Cast Irons, Metall. Trans. A, Vol 11, 1980, p613-620.

Summary of heat treatments carried out on Heat 63.

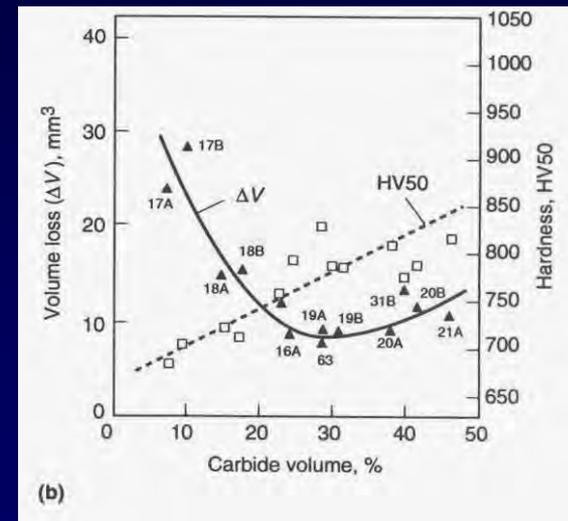
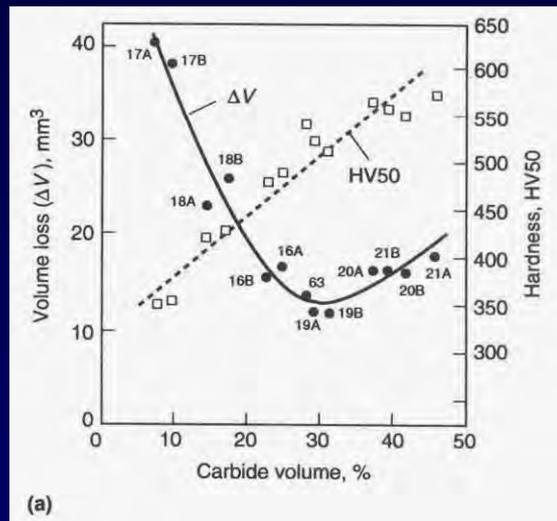


- ❖ Dynamic fracture toughness decreased linearly to a first approximation with increasing volume of carbides.
- ❖ The K_{1d} values were found to be lower in the martensitic condition than in the austenitic condition at the same carbide volume.

Dynamic fracture toughness for austenitic and martensitic matrix irons as a function of volume of massive carbide. Austenitic irons were as-cast, stress-relieved 2 h at 200 °C; martensitic irons were castings heat treated 5 h, at 900 °C, air quenched, refrigerated twice at -78 °C, stress-relieved 2 h at 200 °C.



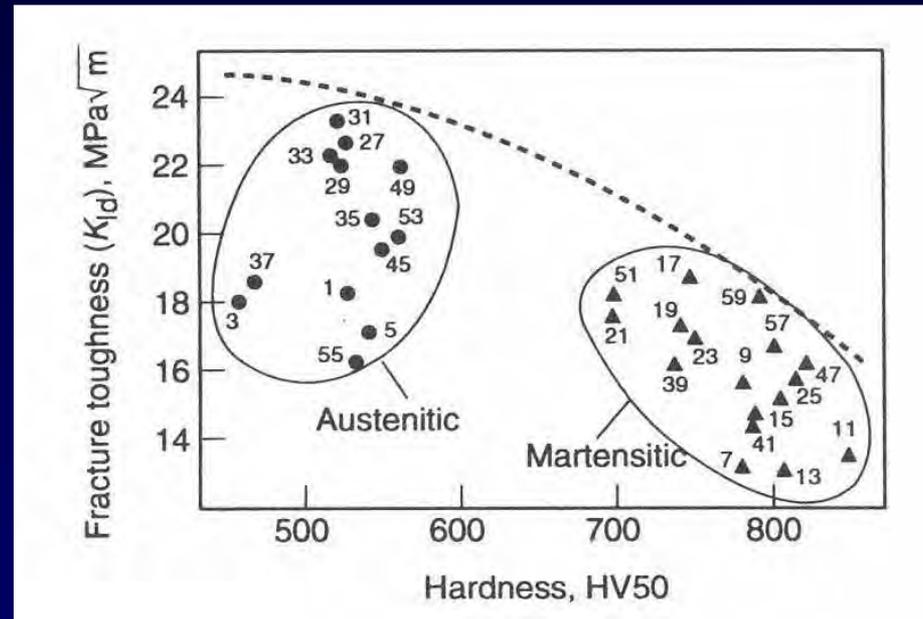
- ❖ Abrasive wear loss decreased with increasing carbide volume up to about 30% in the austenitic condition (a) as well as in the martensitic condition (b).
- ❖ As carbide volumes increased above 30%, however, abrasive wear loss increased with both matrix structures.
- ❖ The bulk hardness of the white cast irons measured on surfaces of rubber wheel test specimens increased with increasing carbide volume linearly to first approximation.



Abrasive wear volume loss and hardness as a function of volume of massive carbides. (a) Austenitic irons (as-cast, stress-relieved 2h at 200 °C). (b) Martensitic irons (castings heat treated 5h at 900 °C, air quenched, refrigerated twice at -78 °C, stress-relieved 2h at 200 °C).

- ❖ A predominantly austenitic matrix resulted in the highest dynamic fracture toughness.
- ❖ Predominantly austenitic as-cast structures, stress-relieved between 200 and 400°C for 2 h, exhibited good dynamic fracture toughness values.
- ❖ Structures heat treated between 950 and 1035°C for 4 h and air quenched, followed by stress relieving at 200°C for 2 h, showed the highest K_{1d} values of the predominantly martensitic structure.
- ❖ The general rule that fracture toughness decreases with increasing hardness was observed, but only to a rough approximation.

- ❖ Different structures with the same K_{1d} value can show large differences in hardness, and, conversely, K_{1d} values can vary substantially at the same hardness.



Dynamic fracture toughness vs. hardness for Heat 63.

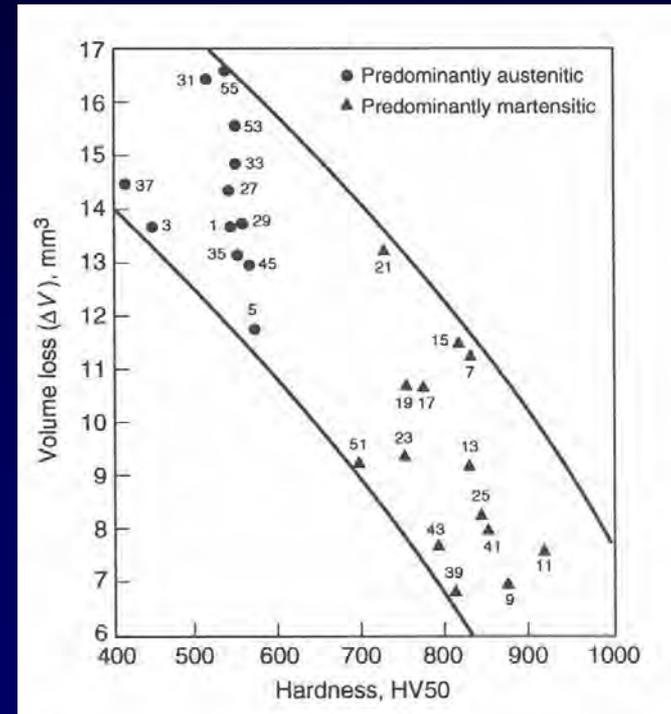
❖ The influence of different matrix structures on the volume loss due to abrasive wear, as a function of bulk hardness as measured in the wet rubber wheel abrasion test.

❖ Highest abrasive wear loss occurred in predominantly austenitic structures that had partially transformed to ferrite/carbide aggregates.

❖ Martensitic structures showed lower abrasive wear loss because of higher hardness.

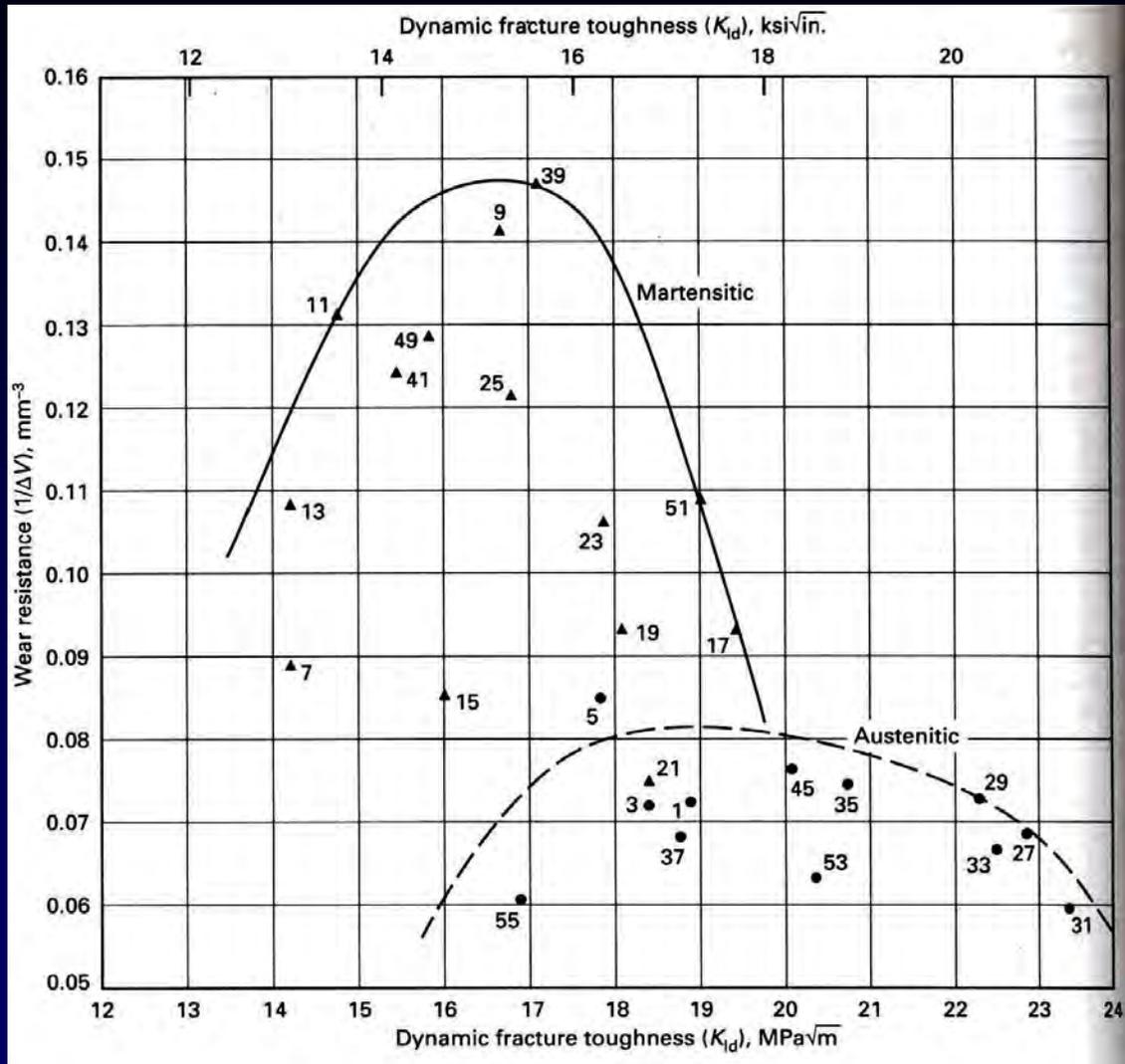
❖ The lowest abrasive wear loss of the predominantly martensitic structures was found for an iron that was heat treated 4 h at 1000°C air quenched, then reheated 3 h at 500°C.

❖ Decreasing abrasive wear loss due to increasing hardness of the structures can be seen only to a first approximation. Similar to the relationship between K_{1d} and hardness, abrasive wear loss can vary considerably at the same hardness for different structures.



Abrasive wear loss vs. hardness of Heat 63.

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- ❖ **The effects of matrix structure and heat treatment on abrasive wear resistance and dynamic fracture toughness.**
 - ❖ **Predominantly austenitic structures showed substantially less abrasive wear resistance.**
 - ❖ **Austenitic structures are the only choice, however if high dynamic fracture toughness is required.**
 - ❖ **Martensitic matrices resulted in much higher abrasive wear resistance, but they can be used only where moderate K_{1d} values can be used.**
 - ❖ **Careful selection of heat treatment (data points 17 and 51) provided both good wear resistance and reasonable fracture toughness.**
 - ❖ **These heat treatments involved air quenching from high temperatures, followed by tempering at 200°C.**

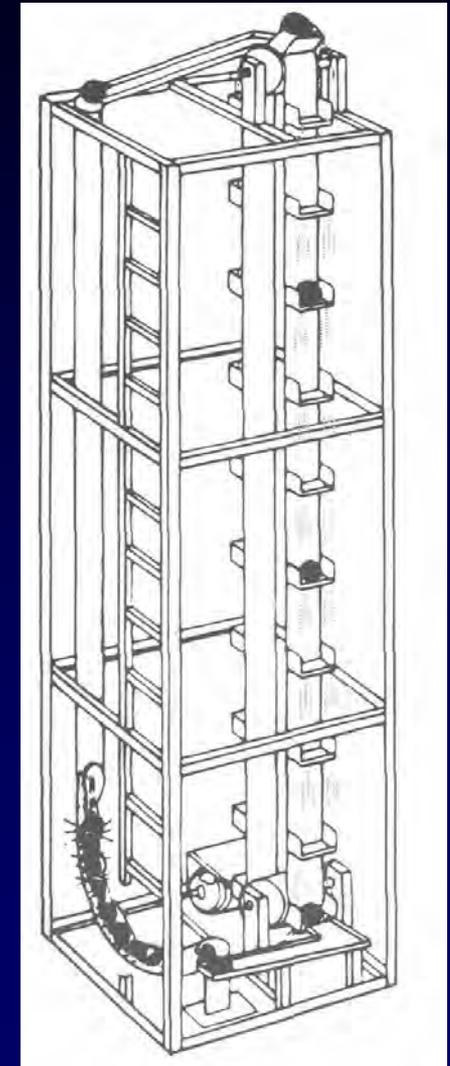


Abrasive wear resistance vs. fracture toughness for Heat 63. The wear resistance is expressed as the reciprocal of volume loss (ΔV).

SPALLING RESISTANCE

- ❖ A study of spalling due to impact of high-chromium white cast iron grinding ball media shows the advantage of careful control of heat treatment. In this test, balls were impacted against each other until they broke or lost 100 g by spalling. The tests were conducted in the ball-on-ball impact-spalling testing machine. The white irons tested had chemical compositions in the following range:

Element	wt%
C	3.00-3.25
Si	0.29-0.34
Mn	0.62-0.67
Ni	0.36-0.46
Cr	16.5-17.7
Mo	1.1
S	0.09-0.11
P	0.05



R. Blickensderfer, J.H. Tylczek, and J. Dodd, The Effect of Heat Treatment on Spalling of a Cr-Mo White Cast Iron, Wear of Materials, American Society of Mechanical Engineers, 1983, p. 471-476.

Ball-on-ball impact-spalling test machine. In this test, 75 mm diam. white iron grinding balls are dropped about 3.5 m to produce multiple impacts on the balls at the base of the curved tube. The energy of the first impact is 54 J. The energy of subsequent impacts decreases to about 5 J at the last impact.

- ❖ The balls were given the heat treatments identified in the following table.

Heat treatment and resulting hardness of chromium-molybdenum white iron grinding balls that underwent impact-spalling tests

See the next table for resulting microstructures.

Type balls	Heat treatment(a)	Hardness, HB
AC	As-cast	415
T1000	As-cast and temper 1000 °F (540 °C)	440
T1100	As-cast and temper 1100 °F (595 °C)	537
T1200	As-cast and temper 1200 °F (650 °C)	486
R1750	Reaustenitize 1750 °F (955 °C)	775
R1850	Reaustenitize 1850 °F (1010 °C)	785
R1950	Reaustenitize 1950 °F (1065 °C)	647
RT850	Reaustenitize 1850 °F (1010 °C) plus temper 455 °C (850 °F)	713
RT900	Reaustenitize 1850 °F (1010 °C) plus temper 480 °C (900 °F)	737
RT950	Reaustenitize 1850 °F (1010 °C) plus temper 510 °C (950 °F)	655
RT1000	Reaustenitize 1850 °F (1010 °C) plus temper 540 °C (1000 °F)	618

(a) Tempering time was 12 h; reaustenitizing time was 4 h. All cooling was in still air. Source: Ref 7

- ❖ The microstructures resulting from these heat treatments are described in the following table.

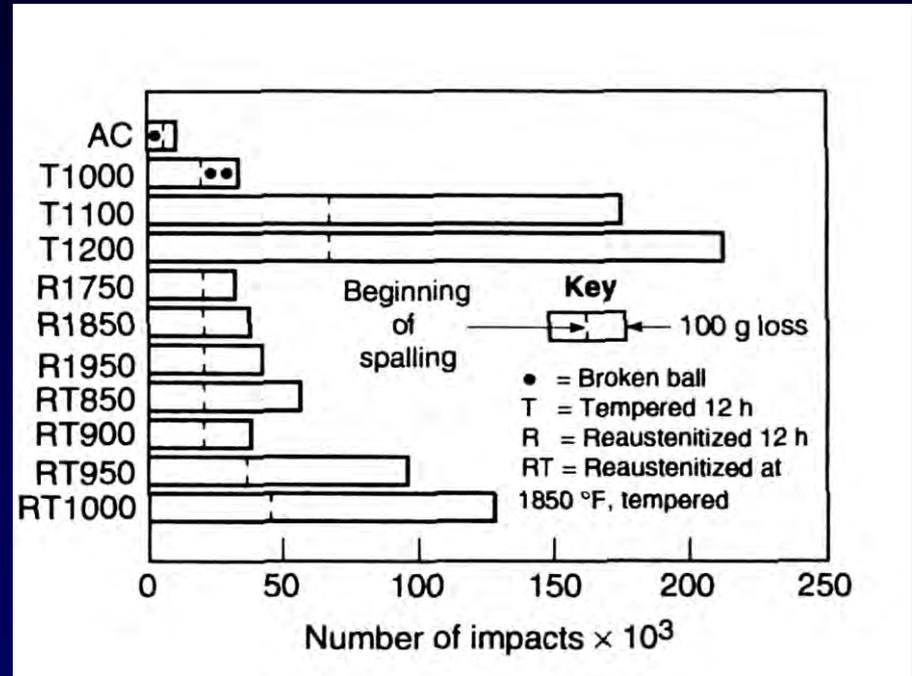
Microstructures of heat-treated chromium-molybdenum white iron specimens after impact testing

See previous table for specimen heat treatment description.

Specimen	Description(a)
AC	Typical white iron hypoeutectic as-cast structure; dendritic austenite; interdendritic Fe-Cr acicular carbides with secondary austenite
T1000	Very similar to above. Interdendritic austenite is beginning to transform.
T1100	Considerable change. Some rounding of dendrites of austenite with interior regions largely transformed to martensite. Most interdendritic austenite has also transformed.
T1200	Slight change from preceding. Prior dendrites of austenite have transformed to martensite. Interdendritic austenite has also transformed.
R1750	Slight rounding of dendritic and interdendritic austenite. Austenite is just beginning to transform.
R1850	Similar to preceding with further transformation of prior austenite
R1950	Similar to preceding with further transformation of austenite. The austenite in prior dendrites has a very fine-grained structure with precipitates on the grain boundaries.
RT850	Overall morphology is similar to that of R1850. Slightly more transformation of austenite to martensite
RT900	Same morphology as above. More transformation to martensite
RT950	Same morphology as above. Essentially all austenite appears transformed to martensite.
RT1000	Same morphology as above. Martensite has decomposed slightly.

(a) Prior austenite that appears transformed by optical microscopy may nevertheless contain some retained austenite. This can be identified accurately only by x-ray analysis. Source: Ref 7

- ❖ The as-cast balls were the shortest lived; one broke at 4544 impacts and the other spalled to 100 g at 8800 impacts.
- ❖ Tempering at 595 or 650°C resulted in a very large increase in 100 g life: 173,000 and 211,000 impacts, respectively.
- ❖ The reaustenitized balls types R1750, R1850, and R1950 spalled quite readily and reached 100 g between 29,400 and 42,900 impacts.
- ❖ R1850 balls were improved by tempering. The longest 100 g life, 127,900 impacts, resulted from the 540°C tempering treatment.



Spalling life of variously heat-treated white iron grinding balls. Life is number of impacts to produce 100 g loss.

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1. G. Laird II, Some Comments on White Cast Iron Microstructures and Wear Properties, Trans. AFS, Vol 1993, p 497-504.
2. F. Maratray and A. Poulalion, "Study of the Hardness of the Martensitic Structures in High-Chromium Ferrous Alloys and the Control and Transformation of Retained Austenite:", Publication M-399E, Climax, Molybdenum Co., 1984.
3. J. Dodd and J.L. Parks, "Factors Affecting the Production and Performance of Thick Section High Chromium-Molybdenum Alloy Iron Castings: Publication M383, AMAX, Inc.

Selected References

- ❖ D.E. Diesburg and F. Borik, Optimizing Abrasion Resistance and Toughness of Steels and Irons for the Mining Industry, Materials for the Mining Industry, Symp. Proc., Climax Molybdenum Co., 1974, p. 26.
- ❖ F. Maratray, Choice of Appropriate Compositions for Chromium-Molybdenum White Irons, Trans. AFS, Vol 79, 1971, p. 121-124.
- ❖ T.E. Norman, A Review of Materials for Grinding Mill Liners, Materials for the Mining Industry, Symp. Proc., Climax Molybdenum Co., 1974, p. 208.

HEAT TREATMENT OF NICKEL-CHROMIUM WHITE IRONS

- ❖ All nickel-chromium white iron castings are given a stress-relief heat treatment because, properly made, they have a martensitic matrix structure, as-cast.
- ❖ Tempering is performed between 205 to 260°C for at least 4 h. This tempers the martensite, relieves some of the transformation stresses, and increases the strength and impact toughness by 50 to 80%.
- ❖ Some additional martensite may form on cooling from the tempering temperature. This heat treatment does not reduce hardness or abrasion resistance.
- ❖ In the heat treatment of any white cast iron, care must be taken to avoid cracking by thermal shock. Never place the castings in a hot furnace or otherwise subject them to rapid heating or cooling. The risk of cracking increases with the complexity of the casting shape and section thickness.

High-Temperature Heat Treatment

- ❖ In the past, hardening of the class I type D alloy, Ni-Hard 4 was performed by supercritical heat treatment when as-cast hardness was insufficient.
- ❖ An austenitizing heat treatment usually comprised heating at temperatures between 750 and 790°C with a soak time of 8 h. Air or furnace cooling was conducted, not over 30°C/h, followed by a tempering/stress-relief heat treatment.
- ❖ Refrigeration heat treatment is the more commonly practiced remedy for low hardness today.

Refrigeration Treatments

- ❖ To achieve a hardness of 550 HB, it is necessary that the as-cast austenite-martensite present. When martensite content is increased to 80 to 90%, however, hardness values exceed 650 HB.
- ❖ To reduce the amount of retained austenite (to form more martensite), deep freeze treatments are commonly applied. Refrigeration to temperature between -70 and -180°C for $\frac{1}{2}$ to 1 h will usually raise the hardness level 100 HB units.
- ❖ A subsequent tempering/stress-relief heat treatment usually follows.



Microstructure of class I type D nickel-chromium white cast iron after refrigeration.

HEAT TREATMENT OF HIGH-CHROMIUM WHITE IRONS

- ❖ Optimum performance of high-chromium white irons usually achieved with heat-treated martensitic structures. Alloying must be sufficient to ensure that a pearlite-free microstructure is obtained in heat treatment.

Minimum alloy content to avoid pearlite in mold-cooled castings for indicated effective section size (plate thickness or radius of rounds)

ASTMA 532 class	Cr(a), %	C(a), %	Plate thickness or radius of rounds		
			25 mm (1 in.)	50 mm (2 in.)	100 mm (4 in.)
IIB, C	14-18	2.0	1.0 Mo	1.5 Mo	1.5 Mo + 1.0 (Ni + Cu)
		3.5	2.0 Mo	2.5 Mo	2.5 Mo + 1.0 (Ni + Cu)
IID, E	18-23	2.0	0.5 Mo	1.0 Mo	1.0 Mo + 1.0 (Ni + Cu)
		3.2	1.5 Mo	2.0 Mo	2.0 Mo + 1.0 (Ni + Cu)
IIIA	23-28	2.0	...	0.5 Mo	1.0 Mo
		3.0	1.0 Mo	1.5 Mo	1.5 Mo + 1.0 (Ni + Cu)

(a) In base irons containing 0.6% Si and 0.8% Mn

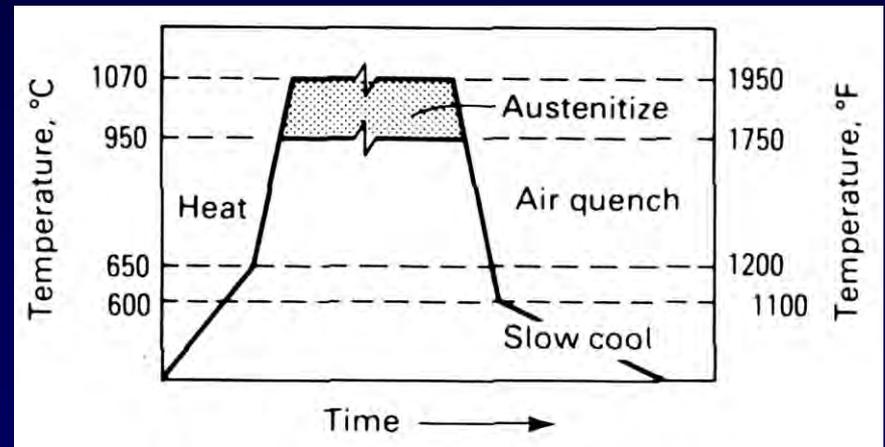
Minimum alloy content to avoid pearlite in heat treatment for indicated effective section size (plate thickness or radius of rounds)

ASTMA 532 class	Cr(a), %	C(a), %	Plate thickness or radius of rounds		
			50 mm (2 in.)	125 mm (5 in.)	150-255 mm (6-10 in.)
IIB, C	14-18	2.0	1.5 Mo	1.5 Mo + 0.5 (Ni + Cu)	2.0 Mo + 1.0 (Ni + Cu)
		3.5	3.0 Mo	2.0 Mo + 1.0 (Ni + Cu)	2.5 Mo + 1.2 (Ni + Cu)(b)
IID, E	18-23	2.0	1.0 Mo	2.0 Mo	2.0 Mo + 0.5 (Ni + Cu)
		3.2	1.5 Mo	2.0 Mo + 0.7 (Ni + Cu)	2.0 Mo + 1.2 (Ni + Cu)(b)
IIIA	23-28	2.0	0.5 Mo	1.5 Mo	1.5 Mo + 0.5 (Ni + Cu)
		3.0	1.5 Mo	1.5 Mo + 0.6 (Ni + Cu)	1.5 Mo + 1.2 (Ni + Cu)(b)

(a) In base irons containing 0.6% Si and 0.8% Mn. (b) Nickel and copper promote retained austenite and should be restricted to combined levels of 1.2% max; manganese behaves similarly and should be restricted to 1.0% max.

- ❖ The heat treatment requires an air quench from the austenitizing temperature. Faster cooling rates should not be used, because the casting can develop cracks due to high, thermal, and/or transformation stresses.
- ❖ Thus the alloy must have sufficient hardenability to allow air hardening. Over-alloying with manganese, nickel, and copper will promote retained austenite, which detracts from resistance to abrasion and spalling.
- ❖ Toughness and abrasion resistance are improved by heat treatment to a martensitic microstructure. The figure illustrates the process and emphasizes the importance of slow heating in a cold furnace to 650°C to avoid cracking.

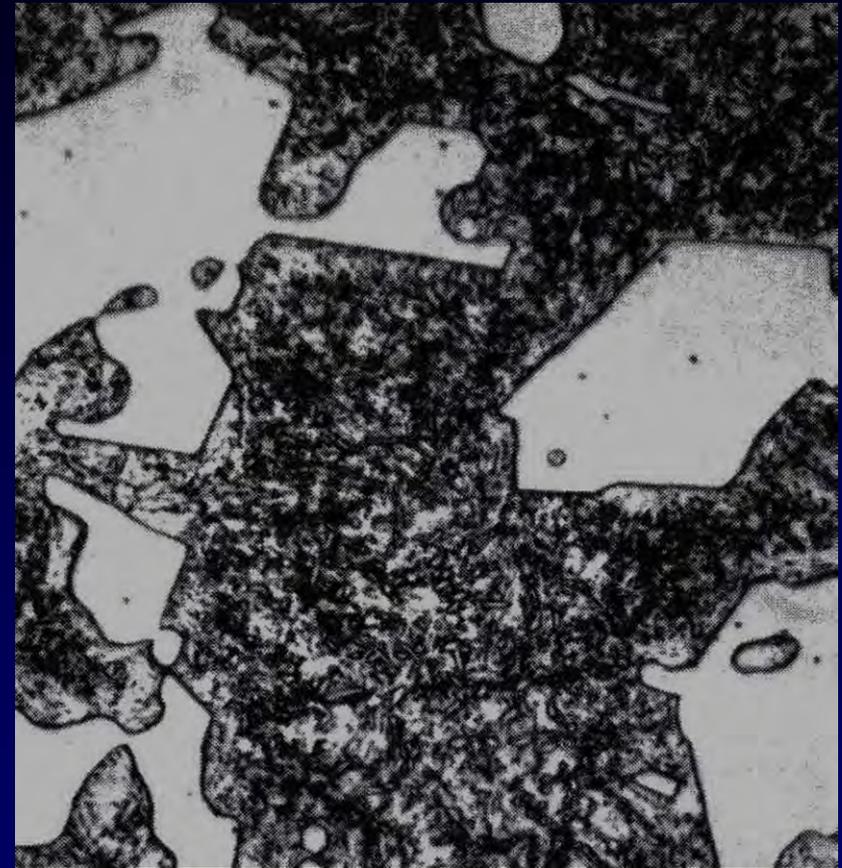
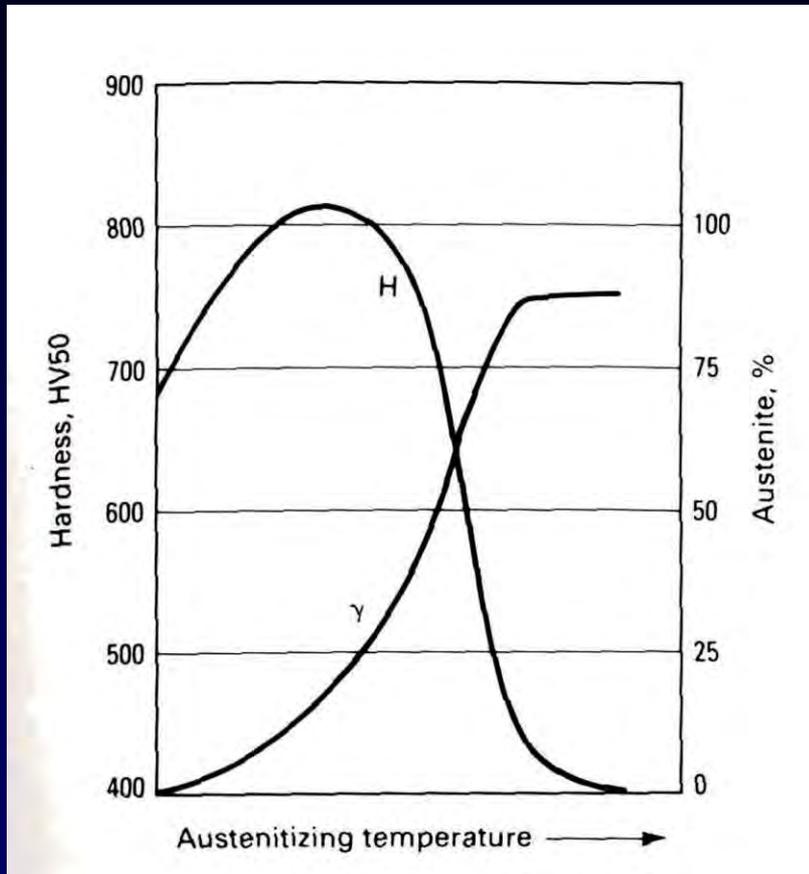
- ❖ For complex shapes, a maximum rate of 30°C/h is recommended. Simple shapes and fully pearlitic castings can be heated at faster rates. The heating rate can be accelerated above red heat.



Heat treatment schedule for hardening high-chromium irons

Austenitization

- ❖ There is an optimum austenitizing temperature to achieve maximum hardness, which varies for each composition.
- ❖ The austenitizing temperature determines the amount of carbon that remains in solution in the austenite matrix.
- ❖ Too high a temperature increases the stability of the austenite, and the higher amount of retained austenite reduces hardness.
- ❖ Low temperatures result in low-carbon martensite, which reduces both hardness and abrasion resistance.
- ❖ Because of this sensitivity to temperature, furnaces that can produce accurate and uniform temperatures are most desirable.
- ❖ The successful heat treatment produces austenite destabilization by precipitation of fine secondary M_7C_3 carbides within the austenite matrix.



Influence of austenitizing temperature on hardness (H) and retained austenite (γ) in high-chromium irons

Microstructure of heat-treated martensitic high-chromium iron illustrating fine secondary M₇C₃ carbides.

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- ❖ **Class II irons containing 12 to 20% Cr are austenitized in the temperature range 950 to 1010°C. Class III irons containing 23 to 28% Cr are austenitized in the temperature range 1010 to 1090°C. Heavy sections usually require higher temperatures within the range.**
 - ❖ **To ensure proper hardening response, castings should be held at temperature long enough to accomplish equilibrium dissolution of chromium carbides. A minimum of 4 h at temperature is necessary. For heavy sections, the rule of 1 h per 25 mm of section thickness is usually adequate.**
 - ❖ **For castings that are fully pearlitic prior to heat treatment, the holding time at temperature can be reduced.**

Quenching

- ❖ Air quenching (vigorous fan cooling) the castings from the austenitizing temperature to below the pearlite temperature range (that is, between 550 and 600°C is highly recommended.
- ❖ The subsequent cooling rate should be substantially reduced to minimize stresses; still-air or even furnace cooling to ambient is common.
- ❖ Complex and heavy-section castings are often placed back into a furnace at 550 to 600°C uniform temperature is reached within the castings.
- ❖ After temperature is equalized, the castings are either furnace or still-air cooled to ambient temperature.

Tempering

- ❖ Castings can be put into service in the hardened (as-cooled) condition without further tempering or subcritical heat treatments. However, tempering in the range of 200 to 230°C for 2 to 4 h is recommended to restore some toughness in the martensitic matrix and to further relieve residual stresses.
- ❖ After hardening the microstructure always contains 10 to 30% retained austenite.
- ❖ Some retained austenite will be transformed following tempering at low temperatures, but if spalling is a problem, higher subcritical temperature tempering can be used to further reduce the austenite content.

Subcritical heat treatment (tempering)

- ❖ Subcritical heat treatment (tempering) is sometimes performed, particularly in large heat-treated martensitic castings, to reduce the amount of retained austenite and increase resistance to spalling.
- ❖ The tempering parameters necessary to eliminate retained austenite are very sensitive to time and temperature, and they also vary with the composition and prior thermal history of the casting.
- ❖ Typical tempering temperatures range from 480 to 540°C and times range from 8 to 12 h. Excess time or temperature results in softening and a drastic reduction in abrasion resistance.
- ❖ Insufficient tempering results in incomplete elimination of austenite. The amount of retained austenite present cannot be determined metallographically.
- ❖ Those experienced with this heat treatment practice have developed techniques, using specialized magnetic instruments, to determine the level of retained austenite after tempering.

Annealing

- ❖ Castings can be annealed to make them more machinable, by either subcritical annealing or a full anneal. Subcritical annealing is accomplished by pearlitizing, via soaking in the narrow range between 690 and 705°C for 4 to 12 h, which will produce hardness of 400 to 450 HB.
- ❖ Lower hardness can often be achieved with full annealing whereby castings are heated in the range 955 to 1010°C, followed by slow cooling to 760°C and holding this temperature for 10 to 50 h, depending on composition.
- ❖ Annealing does not affect the primary carbides or the potential for subsequent hardening.
- ❖ Guidelines for hardening as-cast castings also apply to annealed castings.

Stress Relieving

- ❖ The predominant stresses in heat-treated castings develop as a result of the volume change that accompanies austenite-to-martensite transformation.
- ❖ Low-temperature tempering at 200 to 230°C, is particularly desirable because a substantial improvement (20%) in fracture toughness occurs when tempering the martensite phase.
- ❖ Tempering at temperatures sufficient to significantly relieve stresses (that is, above 540°C) will substantially reduce abrasion resistance.
- ❖ Therefore, it is desirable to minimize the development of transformational stresses via controlled cooling through the martensitic transformation temperature range ($\leq 260^\circ\text{C}$).
- ❖ This is accomplished by slow, controlled cooling to minimize temperature gradients and differential transformation in the casting.

Acknowledgement

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References

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