Lecture 13:
Martensitic Stainless Steels

Mmat 380

Production of Stainless Steels

Types	Major Alloy Additions	AISI
• Ferritic - α	Fe-Cr	4xx
• Martensitic	Fe-Cr-C	4xx
• Austenitic - γ	Fe-Ni-Cr	3xx
• Duplex (α+γ)	Fe-Cr-Ni	
• Precipitation hardened	Fe-Cr-Ni	
• Super ferrites & austenitics	Higher alloy versions of 1 & 3	

Other alloying elements and their purposes

Element	Amount (%)	Purpose
Cr	12-30	Cr_2O_3 – gives stainless character, stabilises α phase
Ni	0-25	Stabilises γ phase (FCC)
Mo	0-9	Reduces pitting and crevice corrosion: stabilises γ-phase
N	<0.5	Reduces pitting/crevice corrosion; stabilizes γ-phase
Ti, Nb	<1	Strong carbide formers; reduce sensitization
C	<0.15 except martensitic grades	Hard martensite for cutting edges; stabilizes γ-phase
Mn	0-12	Ni replacement; stabilizes γ-phase

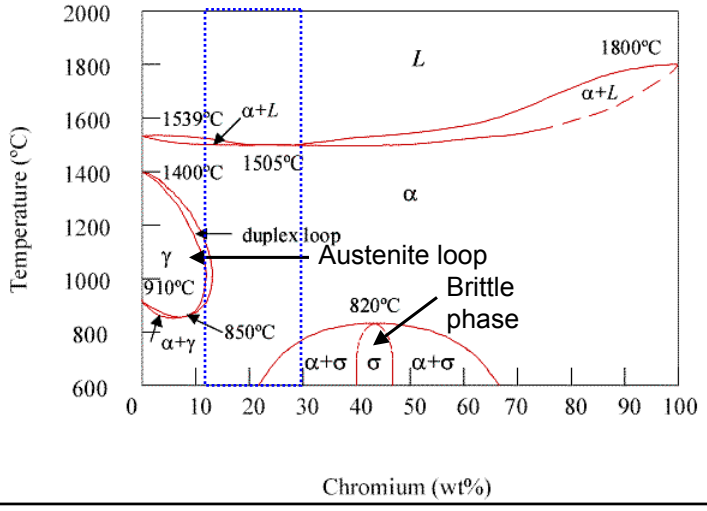
Topics to be covered

- Goal and means to get martensitic stainless steel
- Advantanges and disadvantages
- Applications
- Martensitic compared to ferritic
- Hardness and chemistry
- Effect of temper temperature on corrosion and hardness

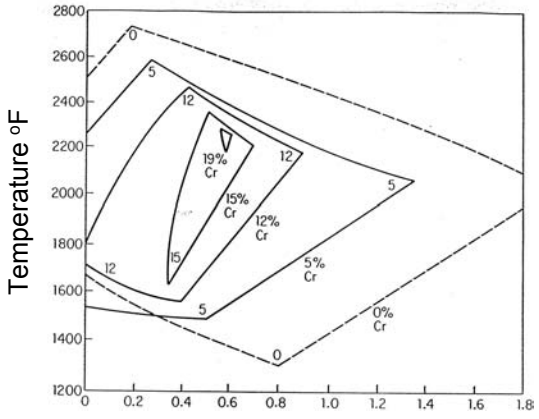
Martensitic stainless steel

- Mechanical properties of the low alloy heat-treatable steels
- Better corrosion resistance
- Get γ-martensite upon cooling
  - Composition must fall in γ loop
  - M_s must remain above room T
  - CCR must remain feasible

Fe-Cr phase diagram

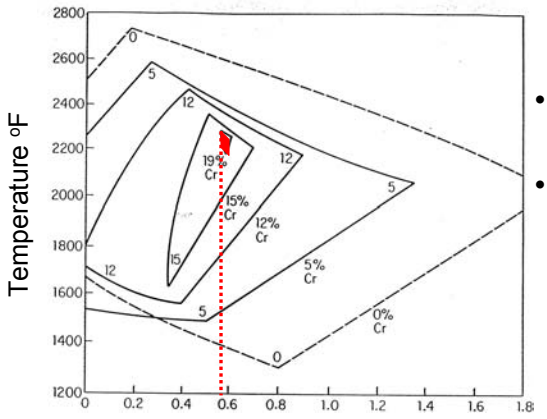


Range of 100% austenite in chromium steels



- 0 %Cr i.e., Fe-C
- Cr shrinks γ field i.e., α stabilizer, raises min. austenitizing T
- > 12 %Cr – must have increasing %C in order to have γ field
- 100% γ field disappears @ > 20 %Cr

Range of 100% austenite in chromium steels

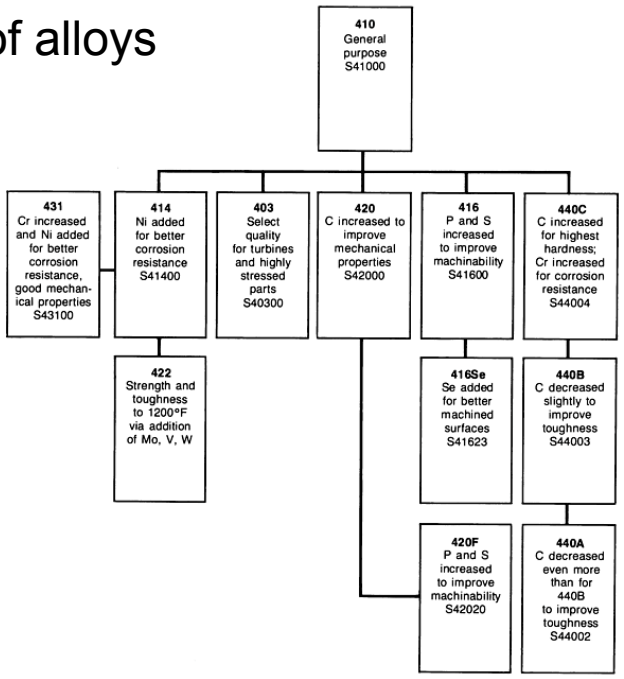


- 19% Cr need a minimum of 0.58 %C
- Temp to form γ ~2100°F (1150°C)

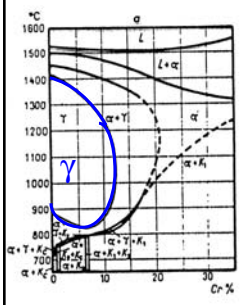
Chemistry requirements:

- In order to be in the γ loop and get Cr passive layer formation need:
- Cr: 12-18%
- C: 0.6-1.2%
- must adjust carbon levels so that when combined with Cr will allow γ to form at elevated temperatures (or γ + carbides)

Family of alloys

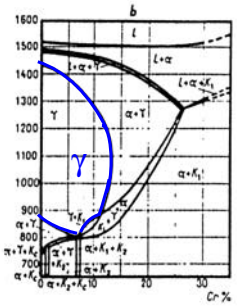


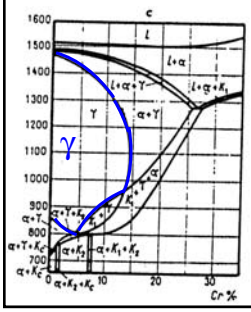
Range of austenite in Fe-C-Cr



a) 0.05%C

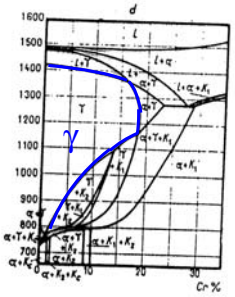
b) 0.1%C





c) 0.2%C

d) 0.4%C

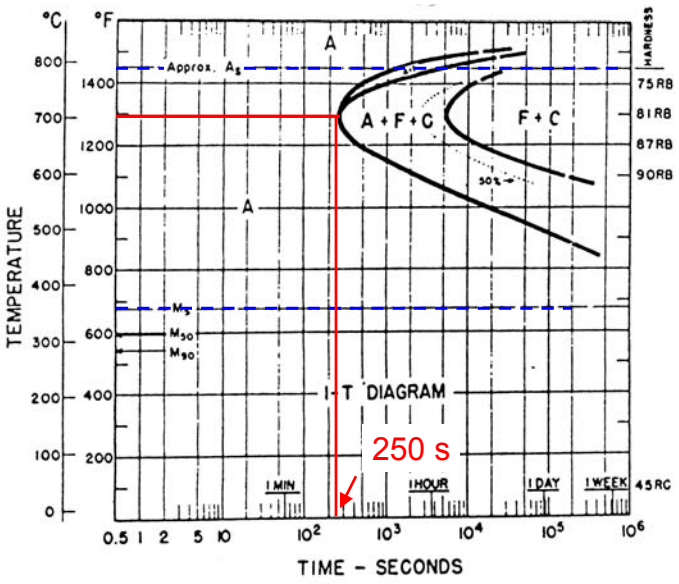


Getting γ-martensite: phase diagram

- As %C increases expands γ loop out and can go to higher %Cr
- Note: Must have sufficient cooling rates to form martensite (I-T diagram)
- Levels of other alloying additions must be limited as we have to be careful that the M_s is not suppressed below room temperature

i.e., Ni ~ 3%; Mo ~ 1%; W ~ 1%; V ~ 0.25%

Getting martensite: IT diagram 410



IT diagram

- Nose at 250 seconds i.e., 4 minutes @ 700°C
  - Therefore can quench harden large sections (i.e., pump shafts etc.) – 4” to full martensite
- Low carbon martensite ~0.1%C max.
- High M_s (350°C) and M_f (250°C)

Pros and cons of martensitic S.S.

Advantages

- High hardness
- Good cutting edge
- Good wear resistance

Disadvantages

- Poorest of all stainless steels in terms of corrosion resistance (relatively low %Cr)

Applications and chemistry

Type 410

- Cr: 11.5-13.0%
- C: 0.15 Max

- Cutlery – turbine blades, pump shafts etc. bolts, nuts, screws
- Higher %C than 409 or 434 therefore martensitic

Type 440 ABC

- Cr 16-18%
- C 0.6-1.2%

- Ball bearings, valves, surgical instruments, knives

Applications

Type 440 C

Inner rings ,outer rings balls

Throwing knife

Ferritic and martensitic stainless steels

	Ferritic					Martensitic	
	430	434	409	406	446	410	440
%Cr	16-18	16-18	16-18	13	23-27	11.5-13	16-18
%C	0.12 max	0.12 max	0.03	0.03	0.03 max	0.15 max	0.6-1.2
Other		1%Mo	0.25% Ni 0.5%Ti	3.0% Al 0.4%Ti			
Applications	Decorative trim		Heat applications				

Hardness and chemistry

- Hardness of martensite depends on %C
- However check 12 %Cr and 18 %Cr diagrams maximum %C in γ at 1100°C (note high γ-temperature)
  - 12 %Cr – 0.55 %C
  - 18 %Cr – 0.30 %C
- Therefore can get higher %C martensite with lower %Cr
  - However higher carbon levels will give more carbides

Effect of 12%Cr on Fe-C phase diagram

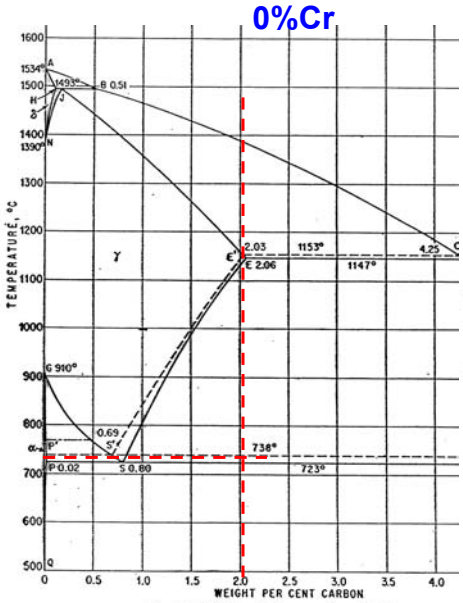
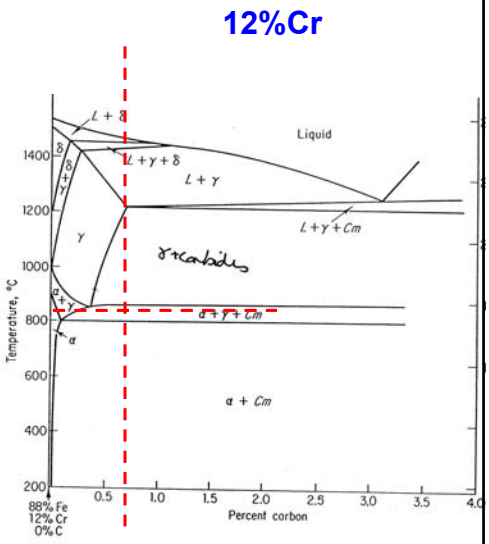
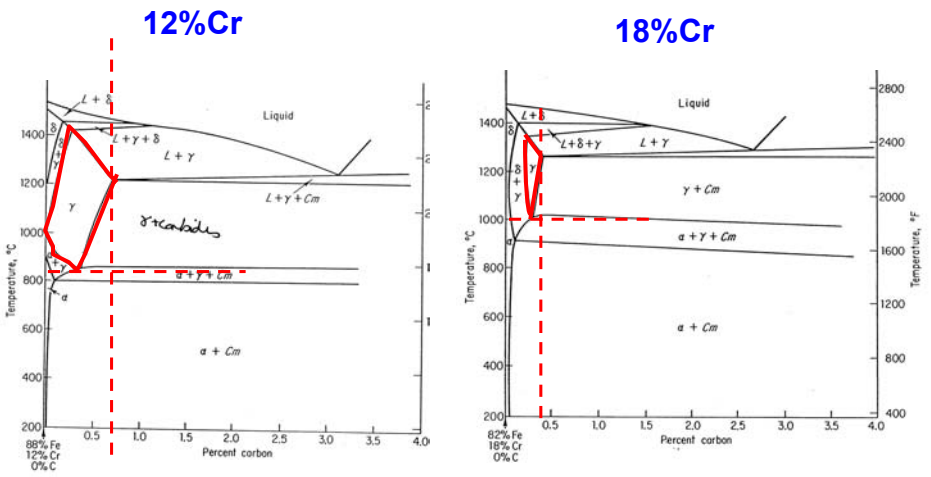


Fig. 201. C-Fe. (Diagram in wt. %.)

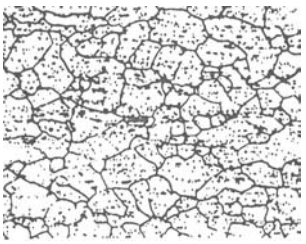


Effect of %Cr on Fe-C phase diagram



12%Cr

- Ferritic: 409
- Annealed ferritic



- Martensitic: 410
- Air cooled and tempered

- could have up to ~0.5 %C and still have 100 % γ
- if > 0.5 %C still have γ + carbides

18%Cr

- Ferritic
- < 0.1 %C
- i.e. 430
- 0.2 – 0.4 %C – 100 % γ

- Martensitic
- 0.4 %C - γ + free carbides
- OK for wear resistance
- i.e. 440

- If increase %Cr must increase %C and vice-versa to avoid δ formation in castings
- Drastic consequences on rolling and forging
  - •C - γ stabilizer
  - •Cr - α stabilizer

Applications: knives, razor blades, scissors, scalpels

Hardest R_c 60-65

- Difficult to sharpen but maintain edge for a long time
  - Best i.e., Heinkel Knives $100/knife

Run of the mill R_c 45-55

- Easy to sharpen but don't maintain edge for very long
- Continuous sharpening or replacement

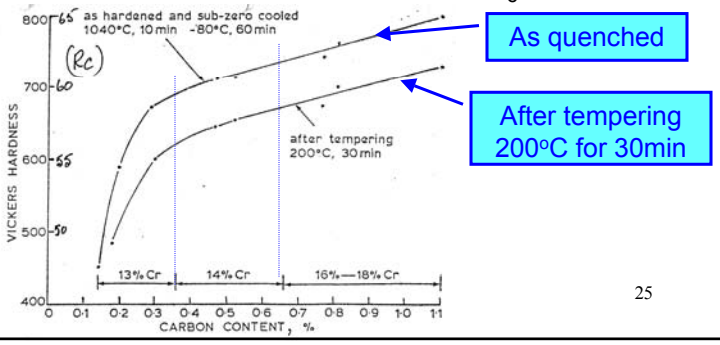
Applications: Knives, Razor Blades, Scissors, Scalpels

Wiltshire and other stainless knives

Razor blades - most scissors

North America	0.12-0.18 %C	47-50 R_c
Europe	0.3-0.45 %C	55-57 R_c

Note: as ⇧ Cr must ⇧ C



Applications: cutlery

- Above tempering is too low – might soften when grinding to re-sharpen
- Some manufacturers temper @ 500°C to R_c 61
  - In USA – carbon contents of table knife steel has been reduced from 0.3-0.12 %C – Heat treated to R_c 47
  - Europe – Generally prefer 0.45 %C R_c 57
  - England – 0.3 %C – R_c 55

440C for high quality butcher knives, hunting knives etc. R_c 61

Cutlery

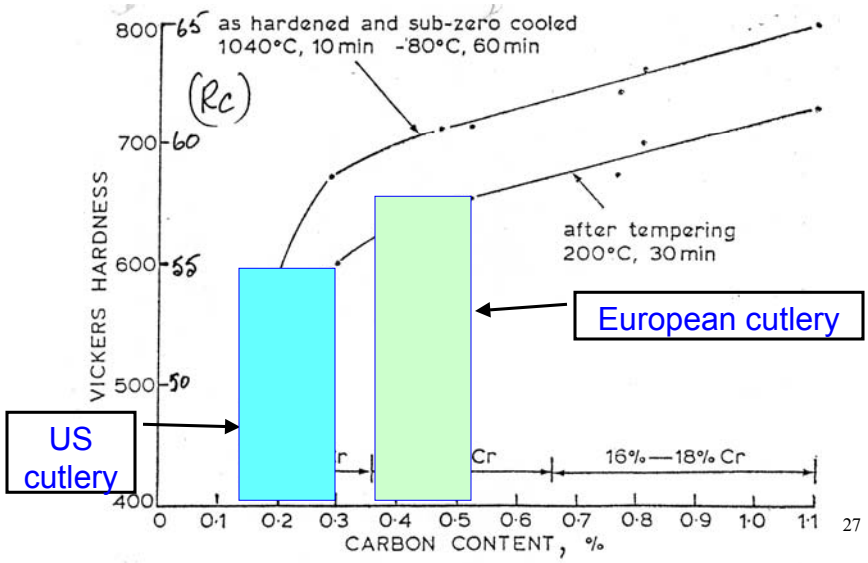


TABLE 7-4
Chemical compositions and typical applications of wrought martensitic stainless steels†

AISI type	% Cr	% C	% Ni	% Mo	% V	% W	% Other‡	Typical applications
403	12.2	0.15 max						"Turbine quality" grade. Steam turbine blading and other highly stressed parts including jet engine rings.
410	12.5	0.15 max						General-purpose heat-treatable type. Machine parts; pump shaft; bolts; bushings; coal chutes; cutlery; finishing tackle; hardware; jet engine parts; mining machinery; rifle barrels; screws; valves.
414	12.5	0.15 max	1.8					Higher carbon modification of type 410. Cutlery; surgical instruments; valves; wear-resisting parts; glass molds; hand tools; vegetable choppers.
420	13	Over 0.15						High-hardenability steel. Springs; tempered rules; machine parts; bolts; mining machinery; scissors; ships belts; spindles; valve seals.
422	12	0.22		1.0	0.25	1.0		High strength and toughness at service temperatures up to 1200°F. Steam turbine blades; fasteners.
431	16	0.20 max	1.8					Special-purpose hardenable steel used where particularly high mechanical properties are required. Aircraft fittings; beater bars; paper machinery; bolts.
440A	17	0.72						Hardenable to higher hardness than type 420; with good corrosion resistance. Cutlery; bearings; surgical tools.
440B	17	0.85						Cutlery grade. Cutlery; valve parts; instrument bearings.
440C	17	1.07						Yields highest hardnesses of hardenable stainless steels. Balls, bearings; races; nozzles; balls and seats for oil well pumps; valve parts.

† After "ASM Databook," *Met. Prog.*, mid-June 1979, vol. 116, no. 1.
‡ S:0.030% max; P: 0.040% max; Si: 1.00% max.

Lower Cr

Max Rc~45

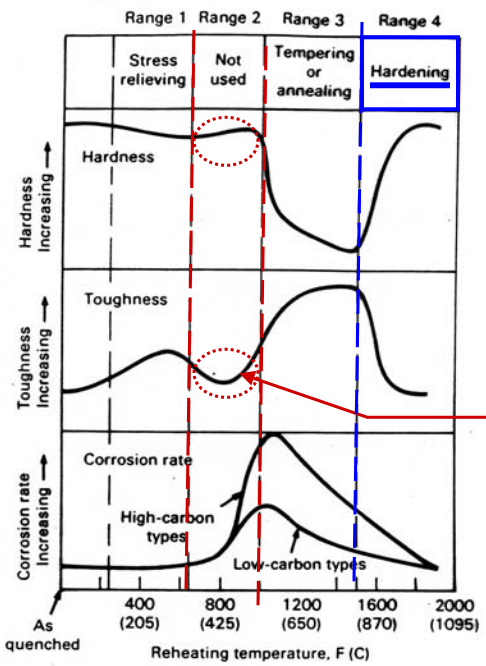
Higher Cr

Max Rc~60

Table 7-4

Note: Ni added for 3 reasons:

- Improve corrosion resistance as it permits a higher Cr content
- Enhance toughness
- Increase hardenability



General trends in relation to aging/tempering temperature for martensitic stainless steels

Temper embrittlement

Aging: Hardening

- Subzero quench will transform most retained austenite
- Significant quantities of retained γ if %C greater than 0.35%
- Austenitizing temperature usually set at 1040°C
- Therefore increased carbon content and chromium levels in γ and thereby decrease M_s and M_f

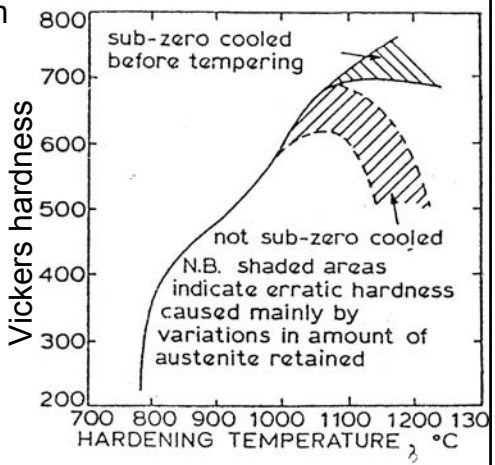


Fig. 4—Sub-zero treatment (—80°C for 1 hour) —Effect on Vickers hardness (aftertempering at 200°C for 30 minutes) 0·45% C, 14·0% Cr, 0·4% Mo.

Austenitizing temperature

- Increased γ- temperature: chromium carbides gradually re-dissolve
- Up to mid-eighties austenitizing temperature usually 950°C now usually set at 1040°
  - Raised from 975-1040°C can see that this increased hardness by 125-180 points H.V.
- If no sub-zero quench then hardness decreases with increased γ above 1050°C

Fe-C phase diagram (12 %Cr)

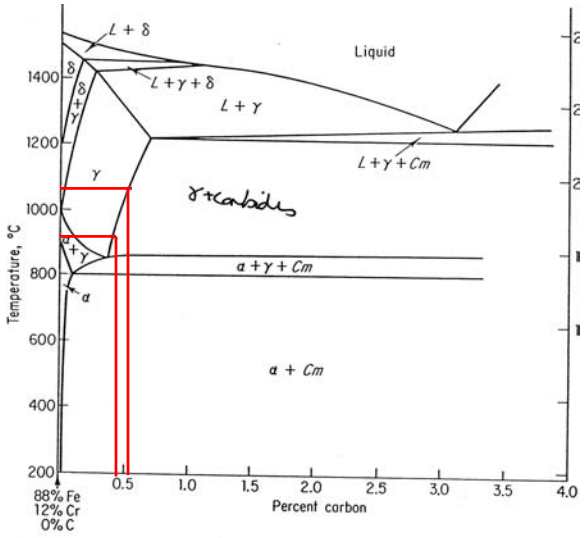
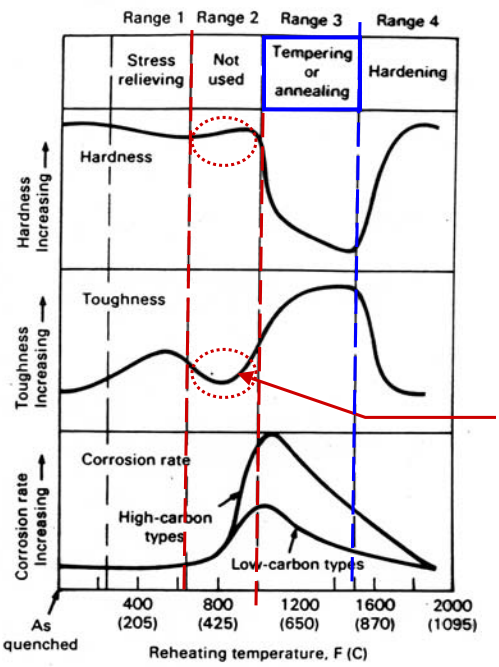


TABLE 7-5
Typical tensile properties of AISI standard martensitic stainless steels in the annealed and tempered conditions

AISI type	Tempering temperature °F	Tempering temperature °C	Yield strength (0.2% offset) ksi	Yield strength (0.2% offset) MN/m²	Tensile strength ksi	Tensile strength MN/m²	Elongation in 2 in (50.8 mm), %	Reduction of area, %
403, 410,	None (annealed)		40	275.8	75	517.1	30	65
416, 416Se	400	204	145	999.8	190	1310.1	15	55
	600	315	140	965.3	185	1275.6	15	55
	800	426	150	1034.3	195	1344.5	17	55
	1000	538	115	792.9	145	999.8	20	65
	1200	648	85	586.1	110	758.5	23	65
	1400	760	60	413.7	90	620.6	30	70
414	None (annealed)		95	655	120	827.4	17	55
	400	204	150	1034.3	200	1379	15	55
	600	315	145	999.8	190	1310.1	15	55
	800	426	150	1034.3	200	1379	16	58
	1000	538	120	827.4	145	999.8	20	60
	1200	648	105	724	120	827.4	20	70
420	None (annealed)		50	344.8	95	655	25	55
	400	204	200	1379	255	1758.2	10	35
	600	315	195	1344.5	250	1723.8	10	35
	800	426	200	1379	255	1758.2	10	35
	1000	538	145	999.8	170	1172.2	15	40
	1200	648	85	586.1	115	792.9	20	55
431	None (annealed)		95	655	125	861.9	20	60
	400	204	155	1068.7	205	1413.5	15	55
	600	315	150	1034.3	195	1344.5	15	55
	800	426	155	1068.7	205	1413.5	15	60
	1000	538	130	896.4	150	1034.3	18	60
	1200	648	95	655	125	861.9	20	60
440A	None (annealed)		60	413.7	105	724	20	45
	600	315	245	1689.3	265	1827.2	5	20
440B	None (annealed)		62	427.5	107	737.8	18	35
	600	315	270	1861.7	280	1930.6	3	15
440C	None (annealed)		70	482.7	110	758.5	13	25
	600	315	275	1896.1	285	1965.1	2	10

Table 7-5

Tensile properties



General trends in relation to aging/tempering temperature for martensitic stainless steels

Temper embrittlement

Effect of tempering temperature on corrosion resistance and hardness

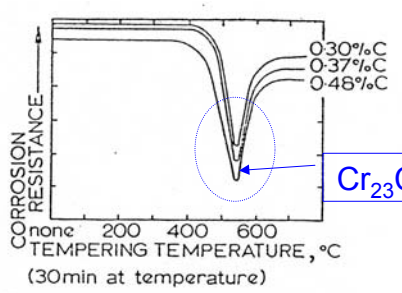


Fig. 7—Tempering temperature—Effect on corrosion resistance of 13·0% Cr steels (hardened from 1040°C) with various carbon contents.

- Can temper at 200-525°C and get same hardness but drastic loss in corrosion resistance when Cr carbides precipitate into the matrix
- Decrease Cr content of matrix therefore lose stainless character

Effect of Tempering Temperature on Corrosion Resistance and Hardness

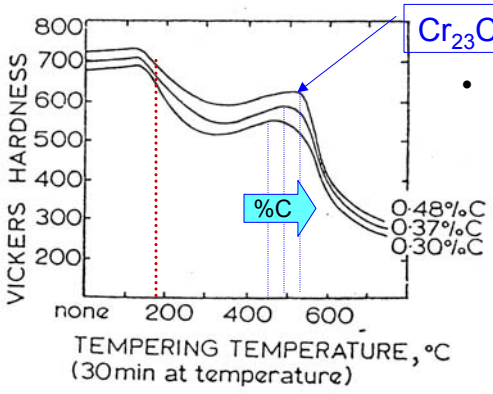
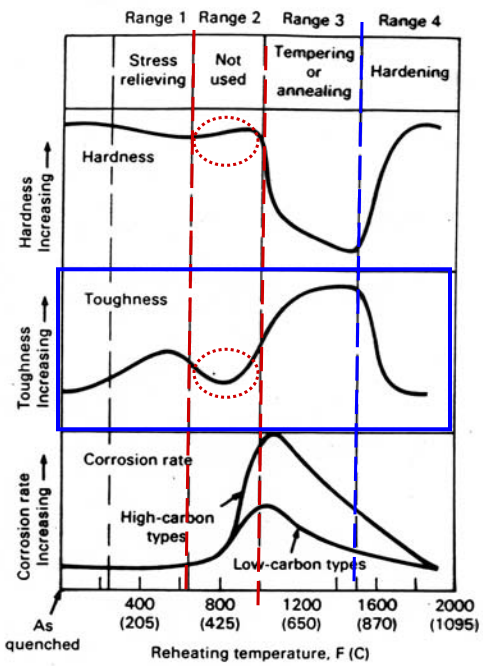


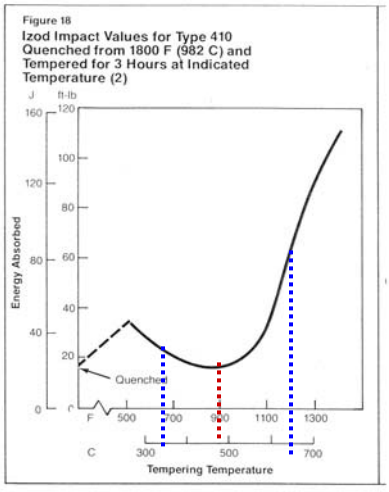
Fig. 8—Tempering temperature—Effect on hardness of 13·0% Cr steels (hardened at 1040°C) with various carbon contents.

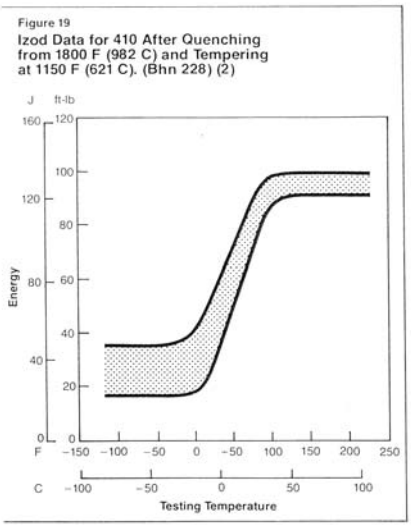
- When sharpening won't over temper edge as long as T < 550°C



General trends in relation to aging/tempering temperature for martensitic stainless steels

Toughness and Temper





Toughness and temper

- Toughness minimum at 500°C
- 2 optimum tempering temperatures:
  - 350°C – higher strength, moderate toughness
  - 650°C – moderate strength, high toughness
- Avoid 500 °C – temper embrittlement (ppt. of carbides and nitrides at the grain boundaries)