Lect.#16
Martensitic Transformations and Strengthening

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• It has long been recognized that some materials can be significantly strengthened by quenching them and inducing the formation of a metastable phase that has a different crystal structure than the parent material.

• One type of phase that can form and lead to significant increases in strength is called martensite. Named after German metallurgist Adolf Martens described a hard microstructure found in quenched carbon steel.

• The phase transformations in this case are called martensitic transformations.

• More recent emphasis placed on the nature of the phase transformation, which is displacive (not diffusive).

• Martensites invoke several (combined) strengthening mechanisms.

• Martensite is important for more than just its strength. Martensitic transformations are also key elements in *shape memory effect* and the *superelastic effect*.

• Martensitic transformations have been identified in a great number of systems, including pure metals, solid solutions, intermetallic compounds, polymers, and ceramics. But the martensite in steel is the more famous type. Some important systems where Martensitic transformations are known to occur are demonstrated in the table below.

Alloy	Structure change
Co, Fe-Mn, Fe-Cr-Ni	F.C.C to H.C.P
Fe-Ni	F.C.C to B.C.C
Fe-C, Fe-Ni-C, Fe-Cr-C, Fe-Mn-C	F.C.C to B.C.T
Mn-Cu, Ln-Tl	F.C.C to F.C.T
Ti-Mn, Ti , Ti-Mo, Li, Zr	B.C.C to H.C.P
Cu –Zn, Cu-Sn	B.C.C to F.C.T
Cu-Al	B.C.C to distorted H.C.P
Au-Cd	B.C.C to orthorhombic
Zro2	Tetragonal to monoclinic

Martensitic transformations in steel:

• Heating steel to the **austenite (FCC)** region and then cooling it slowly, since as the carbon atoms are able to **diffuse** from the austenite crystals, a **body center cubic** crystal lattice will appear instead of the face center

cubic **(Ferrite+Perlite)**. But by very rapid cooling from the austenite situation, such as would be obtained by water-quenching, the available time for diffusion of carbon atoms may be short, in the other hand , the carbon atoms doesn't able to leave the austenite grain and then a new microstructure appear called **Martensite (distorted BCC)**. This new products are formed by *microstructural shear transformations*.

• When martensite forms, there is **no time** for the formation of **cementite** and the austenite transforms to a highly **distorted form of ferrite** which is super saturated with dissolved carbon. The combination of the lattice distortion and the severe work hardening resulting from the shear deformation processes necessary to achieve the transformation cause martensite to be extremely strong but very brittle.

• There are two reasons for a martensite hardness :

1- A tetragonal lattice doesn't have a slip planes such in a cubic lattice.

A Martensite is a super saturated solid solution (محلول جامد فوق الإشباع) from carbon atoms which is confined in a body center tetragonal crystal lattice, since a cubic lattice of an austenite grain may be deform to transfer to the tetragonal lattice; this deformation lattice (B.C.T) may be the essential reason of very high hardness of martensite. the occurring expansion in a crystal lattice because of martensite formation will generate a high local stresses which cause a plastic deformation in a basic phase therefore the martensite appear as an acicular (ابري) structure .

2- Interstitial carbon atoms will prevent the slip.

The solute atoms (carbon atoms) occupy interstitial sites in the solvent lattice (iron) and that lead to distort the crystal lattice and form a stress fields around the solute atoms, this stress fields will interacts with the stress fields of dislocations. This interact reduces the dislocation velocity, in the other hand, this interact will forms an obstacles to the movement of dislocations.

• Hardness of martensite increases rapidly with carbon content, as the distortion increases (linearly) with the amount of dissolved carbon; and because the distortion is what gives martensite its hardness then this, too, must increase with carbon content.

• Martensite strengthening in steel

The high strength of martensite implies that there are many strong barriers to dislocation motion in this structure. Kelly and Nutting have identified two structures in quenched iron-carbon alloys. The conventional martensite has a **plate structure** with a unique habit (بنية) plane and an internal structure of parallel twins each about 0.1 μm thick

within the plates. The other type of martinsite structure is a **block martensite** containing a high dislocation density of (10^{11}) to (10^{12}) dislocations per square centimeter. Thus, part of the high strength of martensite arises from the effective barriers to slip provided by the fine twin structure or the high dislocation density.

The second important contribution to the strength of martensite comes from the carbon atoms. On rapidly transforming from austenite to ferrite in the quench, the solubility of carbon in iron is greatly reduced. The carbon atoms strain the ferrite lattice and this strain can be relieved by redistribution of carbon atoms by diffusion at room temperature. One result is that a strong binding is set up between dislocations and carbon atoms. Another result is the formation of carbon atom clusters (تشكيل عناقيد من ذرات الكاربون) on {100} planes.

• Although 0.8% carbon martensite is very hard, it is also very *brittle*.

But if you *temper* martensite (reheat it to 300–600°C) you can regain the lost toughness with only a moderate sacrifice in hardness. Tempering gives the carbon atoms enough thermal energy that they can diffuse out of supersaturated solution and react with iron to form small closely spaced precipitates of **Fe₃C**. The lattice relaxes back to the undistorted BCC structure of equilibrium **α**, and the ductility goes up as a result. The Fe_3C particles precipitation-harden the steel and keep the hardness up. If the steel is over-tempered, however, the Fe_3C particles *coarsen* (they get larger and further apart) and the hardness falls.

• Less rapid cooling can give a product called **bainite**,. This is similar to tempered martensite where much of the carbon has come out of solution and formed fine needles of cementite which reinforce the ferrite.

• An area of considerable interest has been the development of thermal-

On cooling, the high temperature phase (austenite) starts to transform to the low-temperature phase (martensite) at M_S and the transformation is complete at M_f. On heating the reverse reaction starts at A_S and finishes at A_f. The A_S and A_f temperatures are higher than the M_S and M_f temperatures. Between the A_S and M_S temperatures, martensite can be formed by deformation.
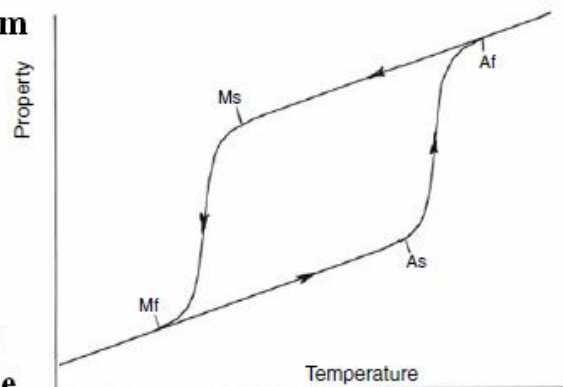
mechanical processes in which martensite is formed from an austenitic matrix which previously had been strengthened by plastic deformation, this process called ausforming. The dislocation density of ausformed martensite is very high (10^{13}cm²) and the dislocations are usually uniformly distributed.
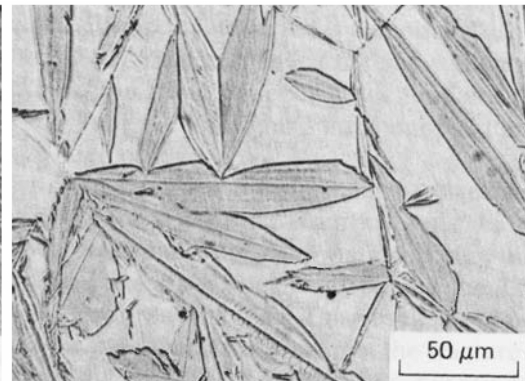
Morphologies of martensite:

The martensite phase can exhibit a variety of morphologies, depending on the composition of the alloy, the conditions in which it is formed, and its crystalline structure. The three most common morphologies are :
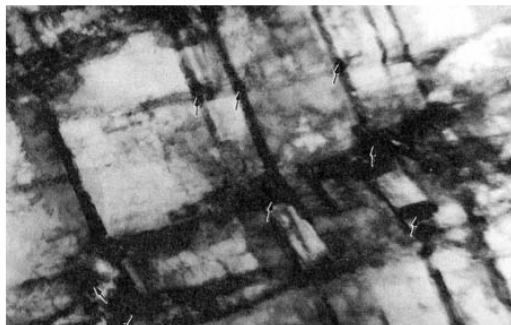- lenticular (lens-shaped)   - Lath martensite
- acicular (needle-shaped)   - Butterfly martensite,
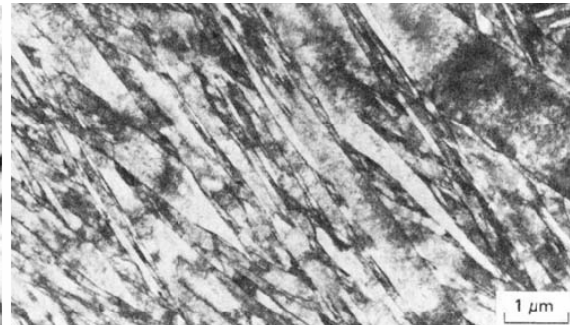-
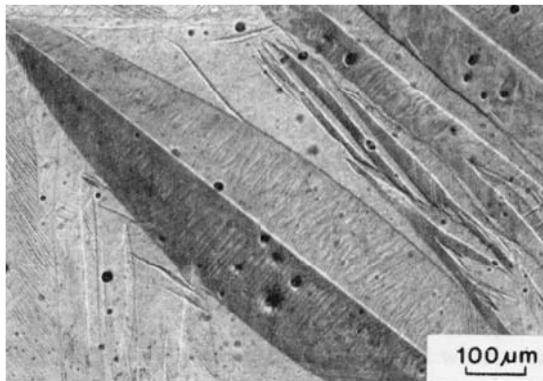
(a) Lenticular martensite in an Fe–30% Ni alloy.   (b) Lenticular (thermoelastic) martensite in Cu–Al–Ni alloy.

Acicular martensite in stainless steel forming at intersection of slip bands
**(c)**

Lath martensite.
(d)

Martensitic strength depends upon a number of factors:
+ Grain size of the Austenite phase from which it forms.
+Solute concentration
- Substitutional solid solution hardening
- Interstitial solid solution hardening
+Precipitation hardening
+Substructure (includes dislocation) hardening

+ Grain size:
• Martensite grain size is determined by the prior austenite grain size.
• Martensite forms in "packets" (bundles) that evolve from shear transformation of austenite grains (e.g., FCC→BCT).
• For normal grain sizes, the yield strength will increase as the martensite plate size or packet size decreases. This is in accordance with the Hall–Petch relationship.
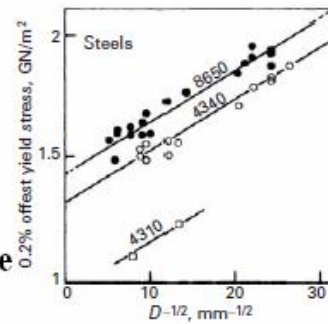
+Substitutional solid solution:
• Substitutional solutes contribute very little (directly) to the strength of ferrous martensites.
• Substitutional solute do contribute indirectly through their effects on grain size, martensite start (Ms) temperature, hardenability, and percent retained austenite.

+Interstitial solid solution:
　　Interstitial solutes (carbon and nitrogen, for instance) can play an important effect. If we regard martensite as a supersaturated solution of carbon in ferrite, a great portion of its strength could be ascribed to solution-hardening. Foreman and Makin developed an equation of the following form to express the effect of the solute concentration C on the shear yield stress of the alloy if only the interaction between dislocations and single-atom obstacles is considered:

$$\tau_0 = \left(1 - \frac{\phi'}{5\pi}\right) G \left(\frac{F_{\max}}{2T}\right)^{3/2} (3C)^{1/2}.$$

Here, $F_{\max}$ is the maximum force exerted by the obstacle on the dislocation, T is the line tension of the dislocation line; G is the shear modulus, and φ- is the angle turned through by the dislocation immediately before it frees itself from the obstacle.

Substructure strengthening of martensite:
• High-carbon martensites have fine twinned substructures. It has been proposed that these structures can provide a major contribution to strength. However, this proposition has been poorly received.
• In lath martensites, which are untwinned but densely dislocated, it has been shown that the increase in dislocation density leads to large increases in strength. Dislocation density can be increased by increasing the carbon content. **Norstrom** has developed the following expression for lath martensite:

$$\sigma_y = \sigma_0 + \sigma_i + k_i \sqrt{d} + \alpha G b \sqrt{\rho_\perp}$$

where

σ_0- Peierls stress, σ_i- Solid-solution hardening effect, k_i- Hall-Petch constant, α- Constant

$$\rho_\perp = \rho_0 + K(C) + \frac{\theta}{b} \cdot \frac{2}{w}$$

Where: w- lath width   c- carbon concentration ρ_0- dislocation density in laths, K- constant, θ - misorientation between laths.

Mechanical Effects:

   A martensite lens introduces macroscopic strains in the lattice surrounding it. The strains introduced by a martensite lens can be decomposed into a dilatational and a shear strain. The dilatational strain is perpendicular to the midrib plane, and the shear strain is parallel to the midrib plane.

The dilatational and shear stresses and strains imposed by the martensitic transformation interact with externally applied stresses, and very special responses ensue. The effects of externally applied tensile, compressive, and hydrostatic stresses are shown in the fig. below.
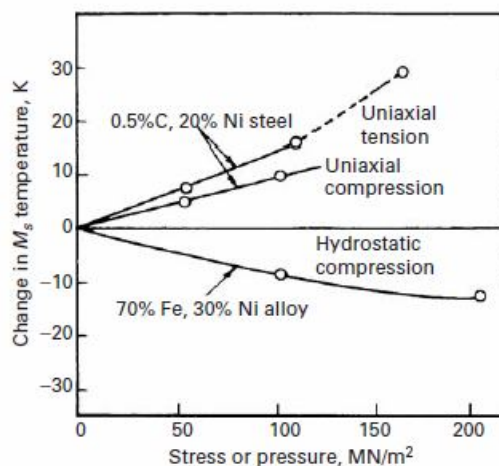
Change in *Ms* Temperature as a function of loading condition.

The uniaxial tension and compression increase *Ms*, whereas hydrostatic compression lowers it. The explanation is that, under the effect of the applied stress, the mechanical work done by the transformation, which can be decomposed into the dilatational and shear components, $\sigma\varepsilon$ and $\tau\gamma$ is either increased or decreased:

$$W = \sigma\varepsilon + \tau\gamma.$$

The hydrostatic stress counters the lattice expansion produced by martensite, but does not affect the shear stress. Hence, a greater amount of free energy is required to trigger the transformation.