ADVANCED METALS

Product design

Products achieve success through a combination of sound technical design and imaginative industrial design. The amalgam creates product character – the way material and processes have been used to provide functionality, usability and satisfaction in ownership.

Technical design focuses on usefulness and efficiency, while industrial design provides emotional pleasure and gives personality to the product.

The product will meet the market if $C < P < V$. C is the cost, comprehensive of production and commercialization, largely determined by technical factors. P is the price, the sum at which the product is offered to the customer. V is the value, a measure of what the consumer thinks it is worth.

The higher the value of the product, the higher can be the price without crashing the relationship.

Product personality is composed of aesthetics, associations, perceptions and emotions, with different degrees of abstraction.

New developments in the field of materials and technologies are inspiration source for the product designer, who is now able to make lighter, cheaper, more functional products.

Metals are heavy but resistant. They are expensive due to the high energetic demand of primary metallurgy, but they can be completely recycled.

Stainless steels

Iron based alloys resistant to corrosion in a wide range of environments and temperatures.

Chromium allows the formation on the surface of a thin and compact oxide layer ensuring passivation and good corrosion resistance. Fe-Cr alloys contain C=0.02-1%, Cr>12%.

The passivating layer is an insoluble Cr oxide layer (Cr2O3). The oxide develops when the steel is exposed to oxygen, water or air. It is very thin and cannot be seen, and reforms very quickly if it is damaged.

Stainless steels undergo sensibilization, pitting, crevice corrosion and are susceptible to acid environment.

The main applications for stainless steels are in food industry, chemical industry, aerospace, surgery, automotive, furniture and design.

Stainless steels are classified as:

- martensitic (Cr=12-19%, C=0.08-1.2%)
- ferritic (Cr=10.5-30%, C=0.015-0.08%)
- austenitic (Cr=16-28%, Ni=6-32%, C=0.02-0.1%)

the production is mainly conduced from scarp in an Electric Arc Furnace, or eventually in a Basic Oxygen Furnace with scrap and pig iron as charge.

In the furnace, oxidation takes place, resulting in processes as decarburization, dephosphorization, elimination of impurities and gases.

Decarburization influences the level of Cr, following the reaction: [C]+(CrO)=[Cr]+CO(gas)

$K_{Cr} = p_{CO}\frac{[Cr]}{[C]}$. The Cr/C ratio is higher reducing pCO.

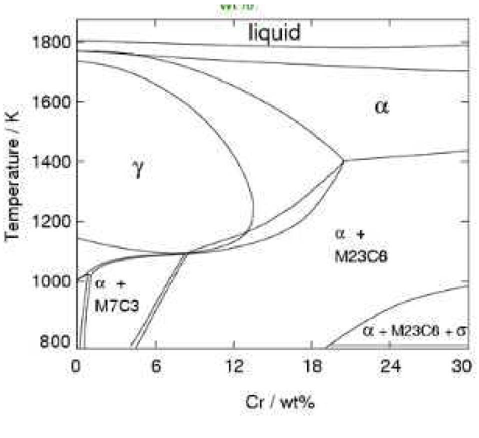
The carbon monoxide partial pressure can be reduced by diluting CO with inert gases like Ar or by vacuum systems (Vacuum Oxygen Decarburization, more expensive).

For high Cr content, a sigma phase can form. At slow cooling rate, this phase precipitates in the ferritic matrix or at grain boundary, causing a deleterious embrittlement.

Cr is an alpha stabilizer ie. promotes the expansion of the ferritic phase field reducing that of austenite at higher temperature. For Cr<13%, alloys can be austenitized and become ferritic on cooling.

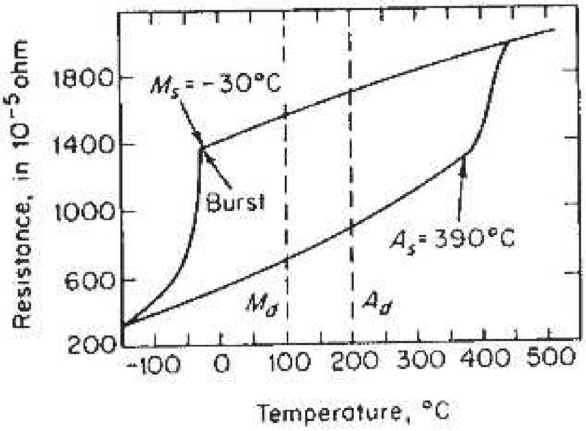
At Cr>13%, alloys are always ferritic and cannot be strengthened by martensitic transformation.

An excessive amount of Cr can eliminate austenite at all temperatures.



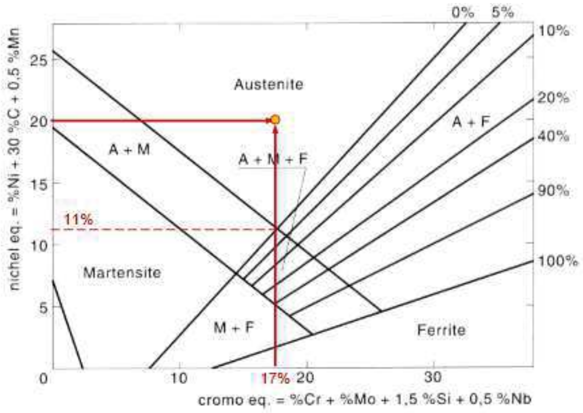
The presence of C induces the precipitation of M23C6 carbides at equilibrium. However, M23C6 is only found after relatively long ageing because it is preceded by intermediate phases in the sequence cementite, M2X, M7C3, M23C6.

Nickel is a gamma stabilizer, promotes the expansion of the austenite phase field, reducing that of austenite at low temperature. Ni induces a strong hysteresis for the transformation (Fe-Ni transformation)



The constitution at equilibrium of ternary Fe-Cr-Ni alloys depends on the relative amount of Cr and Ni. Considering isothermal sections of the ternary phase diagram, it can be observed that the sigma phase is obtained at lower %Cr compared to the binary system.

The addition of other alloying elements provides a further complication. Each element will influence the constitution depending on its specific alpha/gamma stabilizing effect.

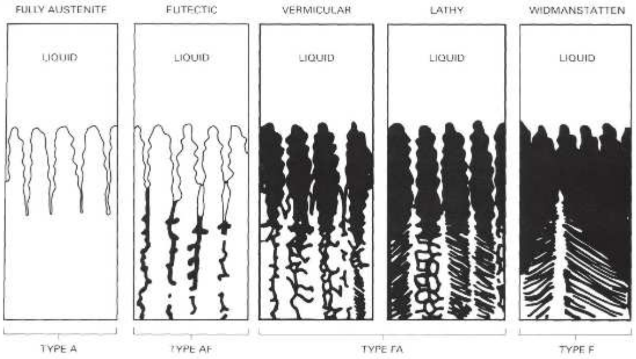


The Schaeffler diagram can be used to predict the structure of as-cast alloys, using suited values of Ni_eq and Cr_eq.

Nowadays thermodynamic modeling is used to calculate diagrams for accurate composition.

At high %Ni, when the alloy solidifies it will form austenite and this phase will be present to room temperature.

At slightly higher %Cr a eutectic is present and the material at first solidifies as austenite but then begins to form some amount of ferrite at the dendrite boundaries and the phase transformation continues (Austenitic-Ferritic Stainless steel).



At still higher levels of %Cr, the ferritic-austenitic grades form. These grades solidify as primary ferrite and then undergo an austenite transformation at lower temperatures.

At very high %Cr the material solidifies as delta ferrite and remains ferrite.

The American designation is used to categorize stainless steels.

- 200 series: Chromium, Nickel, Manganese (austenitic)
- 300 series: Chromium, Nickel (austenitic)
- 400 series: Chromium (ferritic)
- 500 series: Cr<12% (martensitic)
- 600 series: precipitation hardening.

At each commercial grade a number is associate in the corresponding series. The AISI designation establishes the range of the chemical composition and the mechanical properties.

Steels with different structure have different properties. The corrosion resistance decreases from austenitic to ferritic to martensitic. For this reason, most of the used stainless steels are of the austenitic type.

AISI 200/300 comprise about 70% of the total production. They are used for flatware, cookware, architecture, automotive etc. these have high strength and toughness, good ductility, can be strengthened by cold working. These have the highest corrosion resistance.

The typical alloy is 18% Cr and 10% Ni, producing the 18/10 stainless.

Low carbon alloys are produced to avoid corrosion problems due to welding.

The most common grades are AISI 304 and AISI 316.

AISI 304 is the classic 18/8 stainless steel, also referred as A2 in accordance to ISO 3506.

AISI 316 is the second most common grade, used for food and surgical stainless steel. Alloy addition of Mo prevents specific forms of corrosion. It is also known as marine grade stainless steel due to its increased resistance to chlorides compared to 304.

AISI 400 are ferritic stainless steels, used for chemical processing, blades, knives, springs, bearings, automotive trim. They contain 10.5-27% Cr, Ni and Mo. They are cheap and show lower strength than 300 series but can be heat treated.

Type 409 is used for car exhausts.

Type 420 is cutlery grade, with excellent polishability. Type 440 can be hardened to 58 HR making it one of the hardest stainless steels.

AISI 500 series is not as corrosion resistant as the other classes but extremely strong and tough as well as machinable, and it can be hardened via heat treatment. High strength structural applications as nuclear plants, ships, steel turbine blades, tools, etc.

AISI 600 have corrosion resistance comparable to 300 series but can be precipitation hardened for increased strength. Mostly employed in the aerospace industry.

AISI 200, 300 are not magnetic as austenite has an FCC structure, 400 and 500 are.

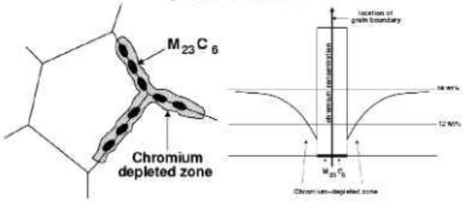
Austenitic stainless steels are austenitized at 1000-1100 °C and relatively fast cooled to retain the austenitic structure. Part of the austenite is metastable and can transform in thermal martensite above Ms and in strain induced martensite below Md.

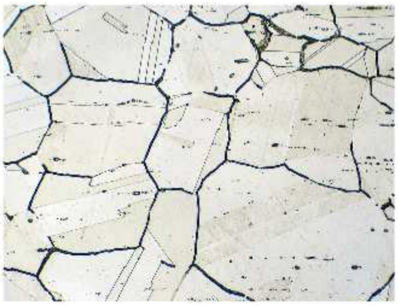
Slow cooling in the range 500-800 °C causes the precipitation of M23C6 carbides (sensitization).

Austenitic stainless steels are susceptible to grain growth without any possibility of recovery by heat treatment. Recrystallization can be obtained by cold working, followed by recrystallization annealing or hot working producing dynamic recrystallization.

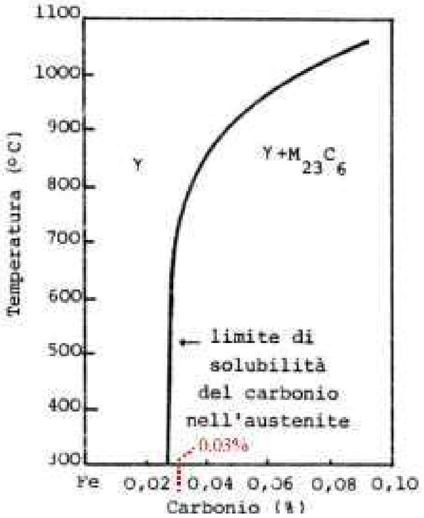
The elastic limit of austenitic SS can be improved by adding C, N, or by cold working. They retain high toughness also at very low temperature, as the austenitic FCC structure does not undergo ductile to brittle transition.

Fig. 5: Mechanism of sensitisation





Sensitized AISI 316



Sensitization is the local Cr depletion due to the precipitation of Cr23C6 carbides. The precipitates absorb chromium from the adjacent austenite causing a localized breakdown in passivity. In these regions -precipitation typically occurs at grain boundary- if Cr<12% the steel becomes prone to intergranular corrosion in aggressive environments.

Prolonged heat treatment makes the steel safe by permitting diffusion to eliminate chromium concentration gradients in austenite.

If the carbon content is below 0.03%, no sensitization occurs as the carbide is not able to form. Low carbon grades indicated by L have improved resistance to intergranular corrosion were developed.

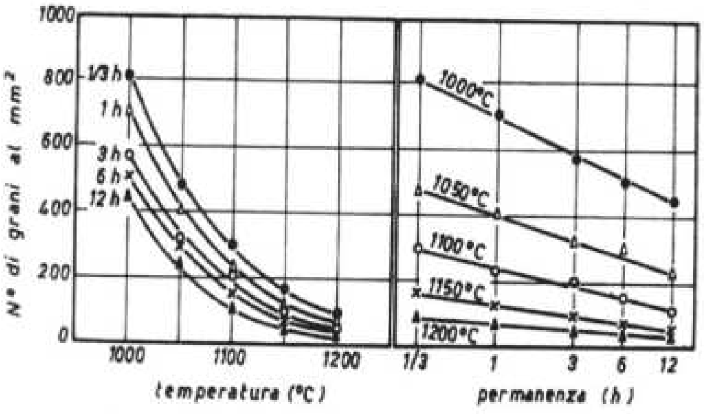
After solubilization at T>1000 °C, the steel must be rapidly cooled down between 800 and 500 °C.

Stabilized stainless steel grades are obtained by adding controlled amounts of alloying elements (Ti, Nb) and following a stabilization heat treatment:

- first solubilization phase to homogenize austenite
- soaking at 885% for 2 hours to produce fine precipitation of alloy carbides

in this way the carbides of other alloying elements precipitate before the precipitation of Cr23C6 and prevent chromium depletion.

Solubilization also allows to eliminate structural modifications induced by previous mechanical working and plastic deformation. The main parameters of the process are solubilization temperature, time and cooling rate. Excessive grain growth can result from high solubilization temperature and/or time.



Stress relieving is carried out by heating at 350-430 °C for 0.5-2 hours and then air cooling to eliminate mechanical stresses which will favor stress corrosion.

Ferritic stainless steels have a microstructure composed of ferrite and carbides at room temperature. Austenite can form upon heating, and martensite can form on cooling.

Additions of Mn and Mo lower Ms below room temperature; Nb and Ti are carbide/nitride formers which reduce the %C in the matrix, contracting the austenite phase field.

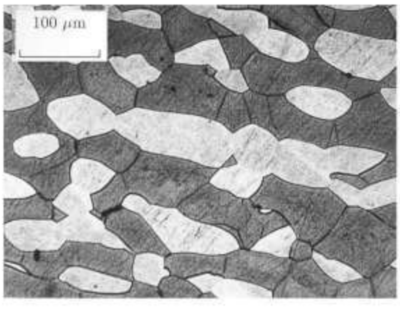
Ferritic stainless steels are more susceptible to grain growth than austenitic due to the inherently higher mobility of atoms in BCC structure.

Ferritic SS show ductile to brittle transition at low temperature. This temperature can be lowered by adding interstitial elements as carbon and nitrogen.

Ferritic SS do not show a1 and a3 points: the only possible heat treatment is stress relieving, which removes stresses due to processing or temperature gradient during welding. The parts are heated to 600-830 °C for 1-2 hours. The upper limit is related to the possible grain growth to which these steels are strongly susceptible. The following cooling must be carried out to avoid soaks in the temperature range between 350-560 which induce embrittlement due to the formation of a Cr-rich alpha’ phase.

The Fe-Cr diagram shows that this phase could also form at T>516 °C together with another brittle phase, the sigma phase, but it requires >50%Cr. The sigma phase reduces toughness, ductility, corrosion resistance. The formation of sigma is favored by high %Cr, %Mo and work hardening induced by cold working.

A steel undergoing sigma embrittlement can be recovered by a solubilization annealing at 900 °C followed by rapid cooling to room temperature.

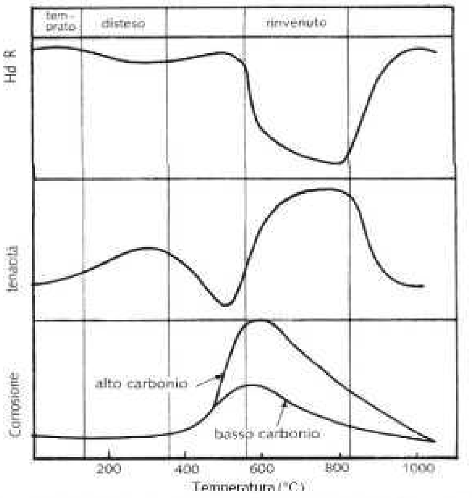


Duplex stainless steel IC381 (dark phase is ferrite).

Duplex stainless steels typically contain 50% austenite and 50% ferrite. The two-phase mixture also leads to a marked refinement in the grain size of both austenite and ferrite. This, together with the presence of ferrite, makes the material about twice as strong as common austenitic steels. They are also less expensive because they contain less nickel.

The two-phase mixture reduces the risk of intergranular cracking during welding.

Martensitic stainless steels have Cr<17%, typically 13%, and C>0.12% to be austenitized and quenched. They show high hardenability and mechanical properties similar to other heat treatable steels.

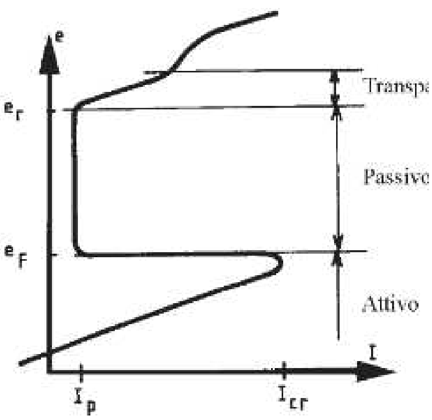


Martensitic SS show A1, A3 above room temperature, so they can be subjected to all kind of heat treatment.

Tempering at 550 °C induces a severe loss of corrosion resistance.

The best corrosion resistance is obtained for T temp < 430 °C, but it yields poor toughness.

The highest toughness is obtained at T temp = 600-760 °C, but the corrosion resistance is lower. The risk of hydrogen embrittlement must be considered in martensitic SS, particularly in those with medium-low C content. This problem can be reduced by carrying out controlled atmosphere heat treatment of by dehydrogenation at 200-300 °C (cheaper).



Stainless steels show high corrosion resistance thanks to the passivating action of a thin Cr_2O_3 layer on its surface. The electrochemical parameters influencing the corrosion resistance of stainless steels are the acidity of the environment, the content of halogen ions, the oxidative potential of the environment, the temperature, etc.

Corrosion can occur anyway if the passive film breaks down, locally or uniformly.

Uniform corrosion can occur in acidic or hot alkaline solutions. The loss by this mechanism can be estimated and allowed for in design. The corrosion rate is very slow when the metal is in passive state.

General corrosion resistance is better at high %Cr, but other solutes can be detrimental. Sulphur is believed to make passivation more difficult, as it alters the temperature dependence of the surface tension of liquid and doing so it increases the penetration during welding.

High %S may be used in free machining SS to help break up the machining chips.

Pitting corrosion is the result of the local destruction of the passive layer and subsequent corrosion of steel. It generally occurs in halide solution. The steel underneath the crack dissolves releasing M+ ions, causing halides Cl- to migrate near the defect by electrophoresis. Even in a neutral solution, this can cause the pH to drop locally to 2/3, not allowing the passive layer to form, as metal ions react hydrolyze water.

The current density in the pit is very large because the anodic region is very small compared to the cathode ie. unpitted steel. This causes the corrosion rate to greatly increase.

Pitting corrosion is favored by inclusions.

PREN (Pitting resistance equivalent number) is an index for pitting and localized corrosion resistance: it varies with type of steel and composition.

Grain boundaries are regions containing a high number of defects and therefore they are more subject to intergranular corrosion.

The formation of martensite makes steels sensitive to cold cracking below 400 °C. This tendency depends on C, H contents. Weldability is improved reducing the C content to 0.15-0.2%, using steels forming austenitic welds, preheating or post-heating before/after welding, carrying out quenching and tempering treatments. A shielding gas should be used during welding to protect against hydrogen absorption.

Ferritic stainless steels show marked tendency towards irreversible grain growth after prolonged exposure above 1150 °C, thus becoming sensitive to intergranular corrosion. The lowest possible welding energy should be used. Post welding heat treatments should be carried out in the welded joint at 750-800 °C to recover a possible quenched martensitic region and to remove sensitized regions. Alloying elements as Ti, Nb reduce the tendency towards grain growth.

Fully austenitic structures are sensitive to hot cracking during above 1100 °C during solidification. Microsegregation is responsible for the accumulation of detrimental low-melting point solute atoms in interdendritic regions, promoting cracking.

Semiferritic grades are insensitive to hot cracking. The addition of ferrite stabilizers allows the formation of about 3-6% ferrite. Ferrite shows higher solubility than austenite for detrimental elements, reducing the formation of low-melting zones. The lower strength at high temperature of ferrite reduces thermal stresses compared to fully austenitic structures.

The use of Schaeffler diagram permits to predict the structure of a welded joint as a function of Ni eq and Cr eq. the diagram resumes the conditions to form ferrite and to avoid the formation of martensite.

Conventional and high strength steels

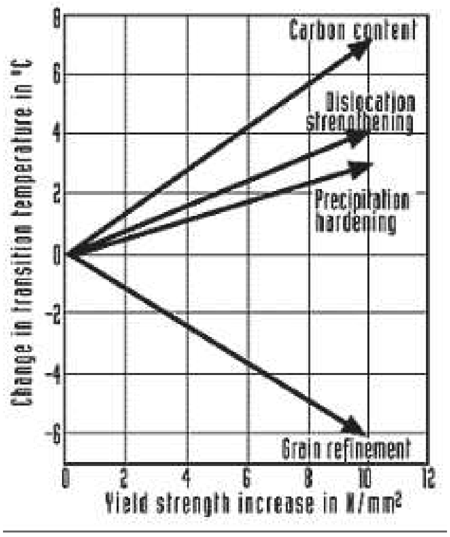
These are economic materials coming from semicontinuous processes as rolling.

Finished products are distinguished as flat (plates or strips) or long (pipes, bars, wires).

These parts are produced often starting from continuous casting, which is the cheapest process, employed for large productions.

There are four main mechanisms to increase the strength of steels:

- Solid solution hardening (%Mn),
- Grain refinement
- Precipitation hardening
- Work hardening



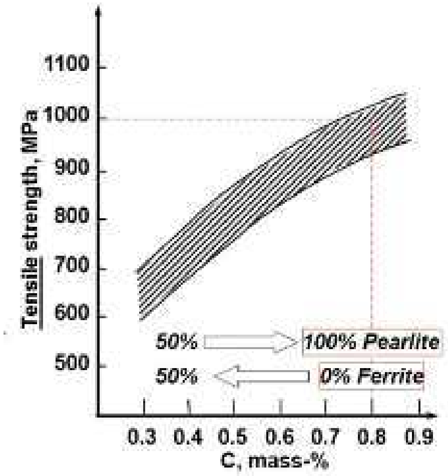
Interstitial free steels: ultra-low C steels strengthened by elements in solid solution, precipitation of carbides/nitrides, grain refinement. They are used for structural and closure applications.

Mild steels: ferritic microstructure, reinforced as IF steels. Drawing quality and Aluminum killer grades are diffuse.

Bake hardenable steels: ferritic microstructure with solid solution strengthening. Carbon stays in solution during steelmaking, comes out at baking temperature increasing yield strength.

C-Mn steels: strengthened by solid solution (Mn)

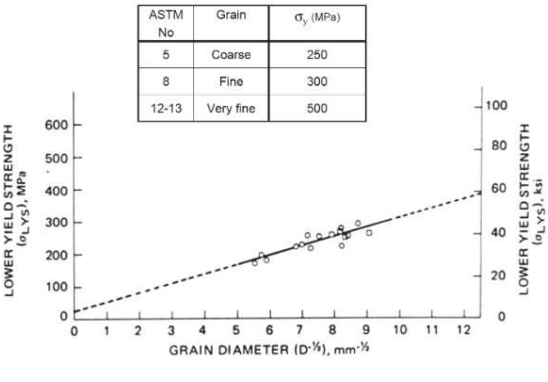
High strength low alloy steels (HSLA): micro alloying elements contribute to fine carbide precipitation and grain size refining.



C-Mn steels have Mn added as ferroalloy, to carry out desulphurization and induce solid solution strengthening. The grades are AISI 10XX.

Increasing %C the strength increases, ductility decreases as %P increases.

Grain refinement increases strength without losing ductility. The strengthening effect is given by Hall-Petch relationship.



ASTM No	Grain	σ_y (MPa)
5	Coarse	250
8	Fine	300
12-13	Very fine	500

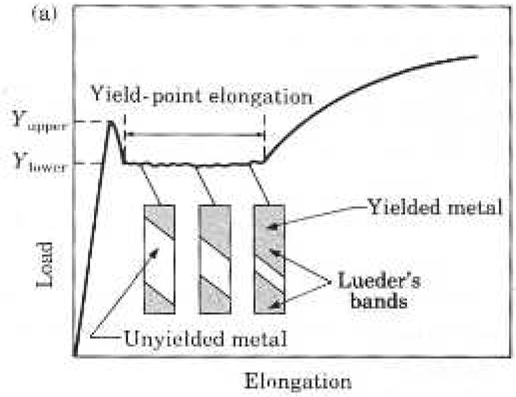
The trend is to have low %C and fine grain size.

ASTM Standards define values for grain size from 5 to 14, and these are related to the yield strength.

In rolling, Luders bands form and uneven the surface of the sheet, bad for aesthetics.

Low C steels (%C<0.1) are used for cold working applications, providing good surface finish.

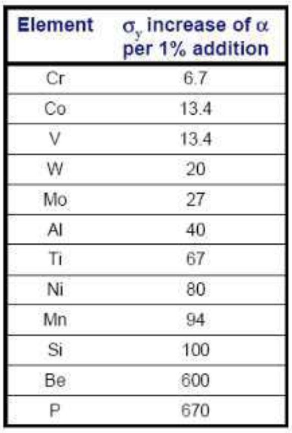
Strain aging in steels with C, N show nonuniform yielding, and this requires temper rolling to get uniform yielding and prevent the formation of Luders bands.



Structural steels typically have C=0.15-0.25%, forming equilibrium structures with 25% ferrite + 0.75% pearlite. After hot rolling, by cooling at higher rate spraying water on the sheets, one obtains finer grain size and a higher amount of pearlite.

To improve the strength, %C, %Mn are increased. An increase of 1% Mn produces a 14% increase in yield strength.

Carbon and manganese bring problems with weldability and brittleness (only carbon).



Element	σ_y increase of α per 1% addition
Cr	6.7
Co	13.4
V	13.4
W	20
Mo	27
Al	40
Ti	67
Ni	80
Mn	94
Si	100
Be	600
P	670

HSLA steels have microalloying elements as V, Nb added to form carbides and nitrides which hinder grain growth and recrystallization. These steels show good strength with excellent weldability and toughness. A very fine grain size is obtained by controlled rolling and cooling: this can increase the yield strength by 100-134 MPa.

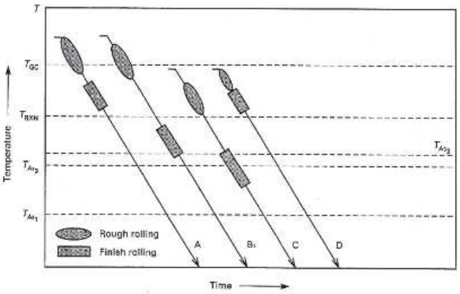
Reducing the finish rolling temperature to 750-800 °C, recrystallization does not occur, yielding finer grain size. When fast cooling, nucleation is faster than growth, so the resulting grain is finer.

The transformation of deformed austenite produces a finer grain size. Increasing Trx makes recrystallization before ferrite formation more difficult.

Small Nb additions (0.04%) delay recrystallization by increasing Trx, and lower forces are required to have deformation because of the presence of austenite.

Controlled rolling is carried out at thicknesses below 1’’, because above this size it becomes difficult to control cooling throughout the section.

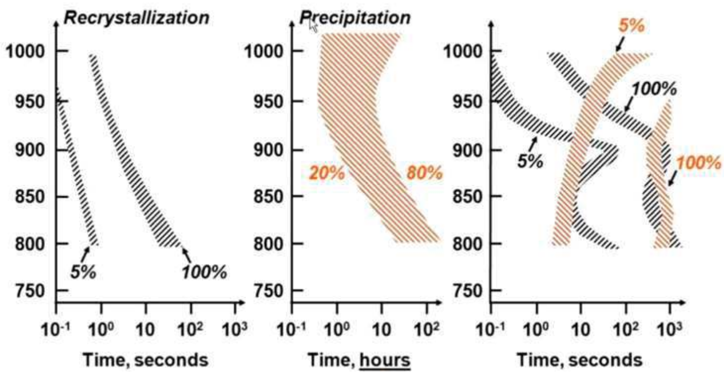
- conventional hot rolling to optimize productivity and reduce costs (1).



- processes designed to achieve large amount of fine-grained ferrite and small fractions of constituents containing cementite which reduces ductility (2, 3, 4).

Plastic deformation of austenite occurs during roughing, and one can have static and dynamic recrystallization, yielding grain coarsening.

In thermomechanical rolling, due to the addition of Nb, the recrystallization temperature increases and thus the treatment can be carried out at higher temperatures without grain growth as rolling becomes easier.

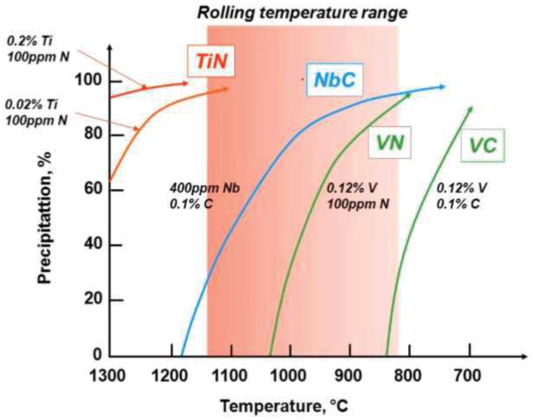


Accelerated cooling yields the transformation of austenitic deformed grains to alpha with high dislocation density, also thanks to Mn which lowers Ac3.

Cooling during coiling is very slow because the center would cool down, but the addition of more hot material makes the cooling process very slow.

Mechanical properties are obtained combining microalloying and processing. HSLA steels which do not undergo controlled rolling show lower ductility than the corresponding C steels.

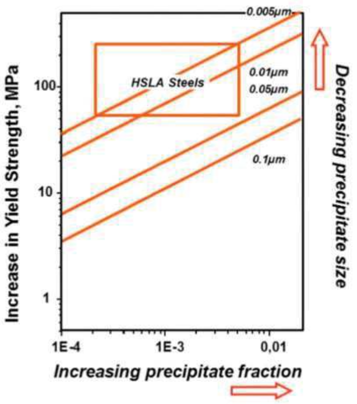
Microalloying elements influence the grain coarsening temperature Tgc, the recrystallization end temperature Trxn, the transformation temperatures Ar3, Bs.



Plastic deformation occurs in preferred sites or bands. Additional nuclei are formed inside the grain thanks to controlled rolling and cooling.

Up to 7 finishing rolling processes are carried out, and all of them take less than 200 s.

The strain-induced precipitation of NbC hinders recrystallization. This occurs in a specific temperature range (around 900 °C), as recrystallization is slower.



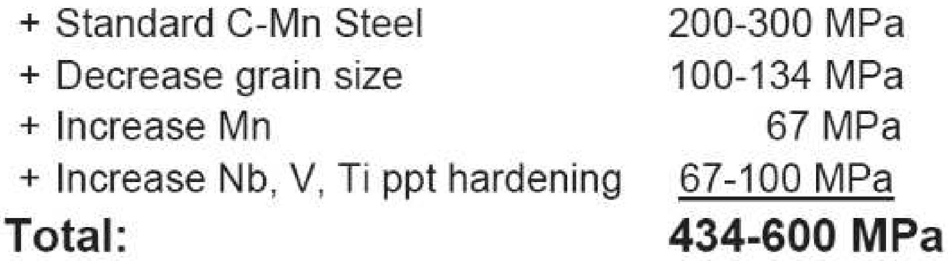
CCT curves of Nb-microalloyed steels are shifted at higher temperature with respect to Nb-free steels, and to lower times.

HSLA have different carbides and nitrides formed. TiN is stable at higher temperature, and it acts as a grain controller during reheating. NbN, NbC precipitate in austenite during rolling, restricting grain growth and retarding recrystallization.

A pancake microstructure is obtained, with nuclei closer together and therefore finer recrystallized grain size. VN, VC precipitate on cooling, after rolling.

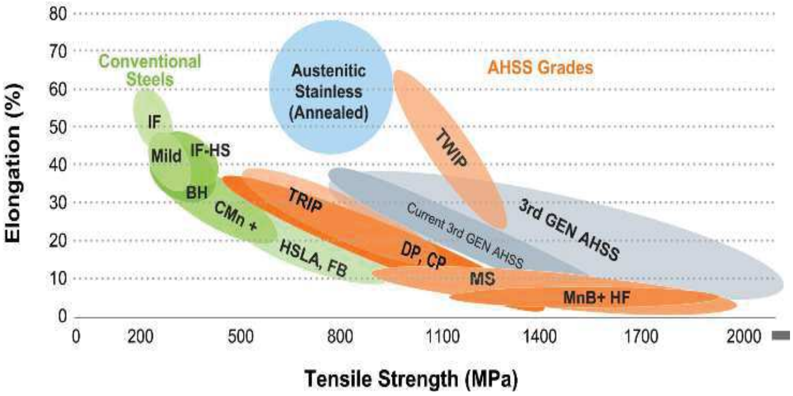
The decrease in precipitate size yields a contribution to the yield strength.

Now it is possible to lower %C and still have about 500 MPa steel.



+ Standard C-Mn Steel	200-300 MPa
+ Decrease grain size	100-134 MPa
+ Increase Mn	67 MPa
+ Increase Nb, V, Ti ppt hardening	67-100 MPa
Total:	**434-600 MPa**

Advanced high strength steels



These are complex materials with carefully selected chemical compositions and multiphase microstructures, resulting from precisely controlled heating and cooling processes.

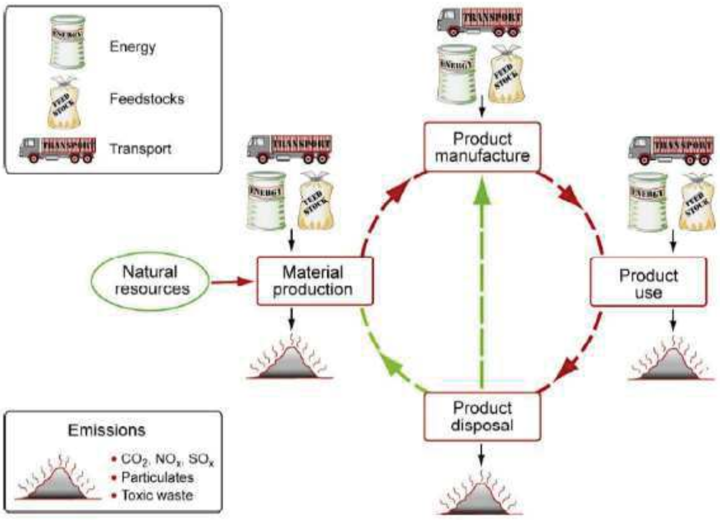
AHSS have yield strength above 550 MPa while ultra-high strength steels have strength above 780 MPa.

AHSS with tensile strength above 1 GPa are often called gigapascal steel.

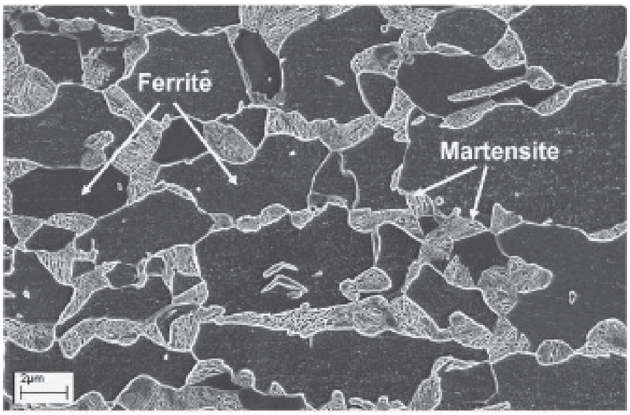
The generic nomenclature is XXX AA/BBB, referring to type of steel, minimum sigma y/ UTS [MPa]

A material showing good formability has a large difference between sigma y and UTS, because forming processes rely on strain hardening, obtained above yield stress.

Steel is preferred to Al alloys for the lower embodied energy. The embodied energy is the fossil fuel energy consumed in making 1 kg of material. The emission of undesired gases for the production of the material is also considered (CO2, NOX, SOX, CH4).



Dual phase steels



DP steels consist of a ferritic matrix containing a hard martensitic second phase in the form of island. They are obtained by controlled cooling from austenite in hot-rolled products, or from alpha+gamma in continuously cold-rolled and hot-dip coated products.

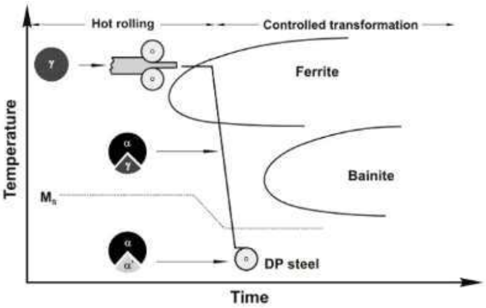
Some bainite and retained austenite may be present depending on the composition (hardenability) and thickness (sheets or plates).

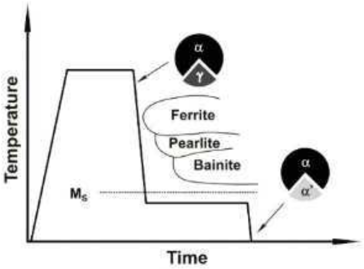
Transforming some austenite to ferrite before a rapid cooling transforms the remaining austenite to martensite.

Composition: Carbon is a gamma-stabilizer, strengthens martensite, determines phase distribution. Manganese is a gamma stabilizer, solid solution strengthener for ferrite, retards martensite formation. Vanadium and Niobium can be added to work at different temperature ranges.

Microstructure: continuous alpha network giving excellent ductility and martensite islands.

Production process:





- controlled cooling from hot rolling. Due to alpha formation, most of the carbon partitions in austenite. A higher carbon content in austenite leads to a lower Ms, so it is more difficult to transform austenite into martensite.

- Controlled cooling from $\alpha + \gamma$ structure of cold rolled products. The cold product is re-heated and quenched to prevent formation of austenite, which then transforms into martensite.

DP steels have higher work-hardening rate than HSLA so that necking is postponed. The strength increases but ductility does not. The ratio UTS/yield is higher than that of HSLA: more complex shapes can be obtained without cracking.

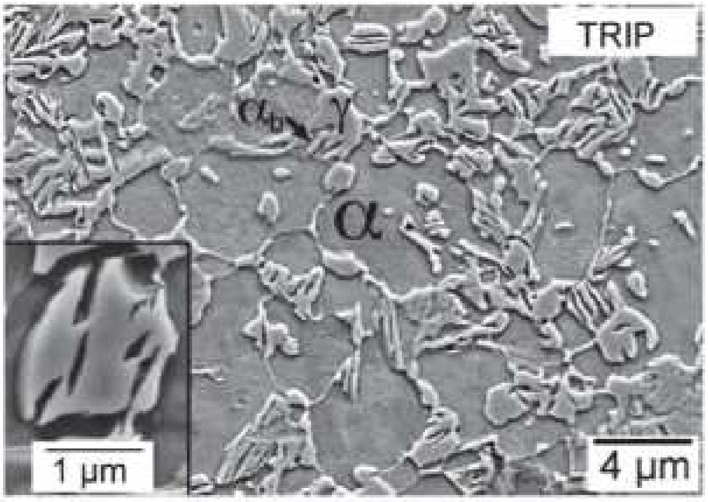
The work hardening rate n is the maximum of the engineering curve.

Transformation induced plasticity steels

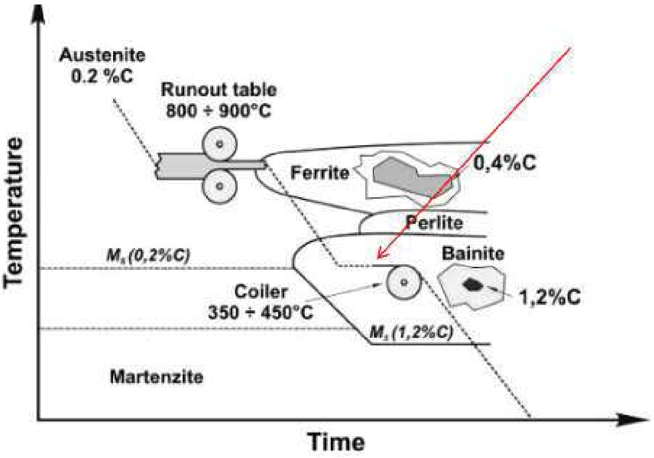
Retained austenite transforms into martensite during plastic deformation. γ_r is finely dispersed in ferrite, so TRIP steels become stronger after the transformation.

Plastic deformation forms martensite nucleation sites in microscopic areas. These are known as shear bands, where crystallographic defects such as twins are located.

Composition: silicon delays carbide precipitation, carbon drops Ms below room temperature.



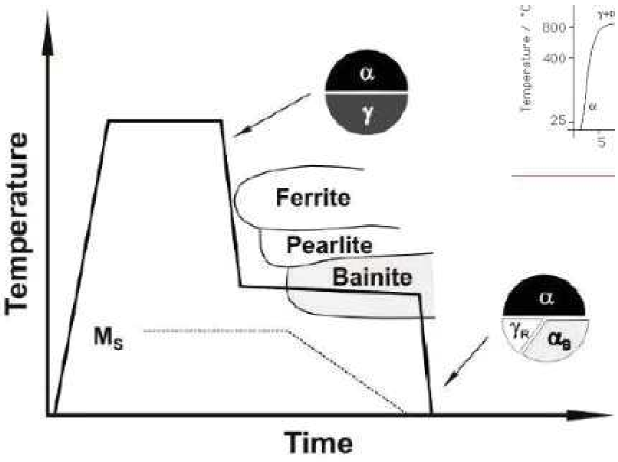
Microstructure: retained austenite embedded in a primary matrix of ferrite. At least 5% γ_r should be present, but also bainite and martensite can be present. We want to retard carbides precipitation as carbides strengthen but lower ductility. The continuous ferrite matrix provides ductility, islands of austenite and some bainite are present.



With Si addition, the reaction of bainite is not $\gamma \rightarrow \alpha + Fe_3C$, because cementite precipitation is delayed, therefore it is $\gamma \rightarrow \alpha_b + \gamma_{high\,\%C}$. Ferritic bainite forms, austenite is richer in carbon, and no carbides precipitate.

Production process: controlled cooling from hot rolling and isothermal hold at an intermediate temperature to produce bainite. Both processes yield carbon enrichment of austenite, lowering Ms below room temperature.

A batch process can be used as for DP steels: starting from $\gamma + \alpha$, isothermal hold in bainite range yields ferrite+ bainitic ferrite + retained austenite. $\alpha + \gamma \rightarrow \alpha + \alpha_b + \gamma_R$



Intercritical annealing is carried out at 780/880 °C then isothermal hold at 350/450 °C. This batch process is optimal for thicker parts.

In TRIP steels, retained austenite progressively transforms to martensite with increasing strain, so the work hardening rate n increases. Work hardening rates of TRIP steels are higher than those of conventional HSS: stretch forming and more extensive deformations can be achieved.

High Si, Al content accelerates the ferrite-bainite formation and assists in maintaining the necessary %C within retained austenite avoiding carbide precipitation.

Different TRIP steel grades are distinguished depending on %C:

- low carbon TRIP steels: retained austenite begins to transform almost immediately after deformation, so n increases during stamping;
- high carbon TRIP steels: retained austenite is more stable and transforms after processing so it remains in the final product and transforms during crashes.

Alloying elements degrade the resistance spot welding behavior. New welding processes must be studied such as pulsating welding or dilution welding.

Complex phase steels

Complex phase steels consist of small amount of martensite, retained austenite and pearlite within a matrix of ferritic bainite. Less stringent cooling practice can be imposed because no retained austenite is required in the microstructure (different than TRIP steels).

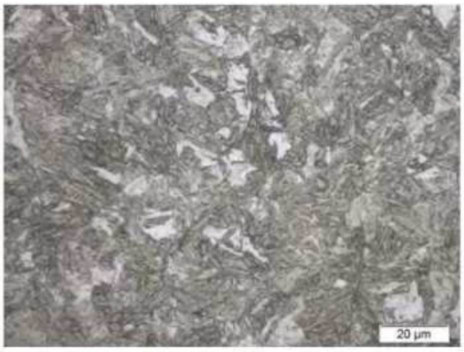
Microalloying with Ti, Nb yields an extreme grain refinement.

Microstructure: continuous ferrite phase providing ductility, islands of austenite and some bainite.

Production process: similar to that of TRIP steel, but with no need for isothermal hold in the bainitic range.

CP steels show UTS > 800 MPa, high energy absorption, high residual deformation capacity and good hole expansion.

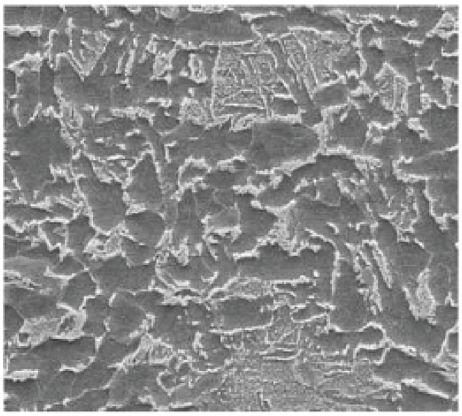
Martensitic steels



Martensitic steels feature a fully martensitic structure obtained by quenching. MS steels have much higher yield strength than the other AHSS, but elongation at break is limited (5%). UTS reaches up to 1700 MPa.

To obtain a fully martensitic structure, low thickness and high hardenability are required.

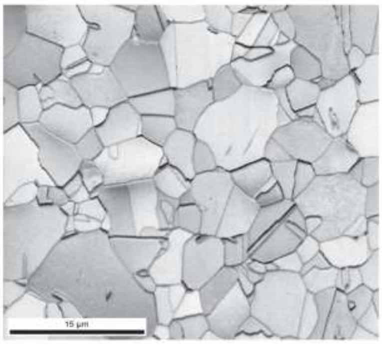
Ferritic-Bainitic steels



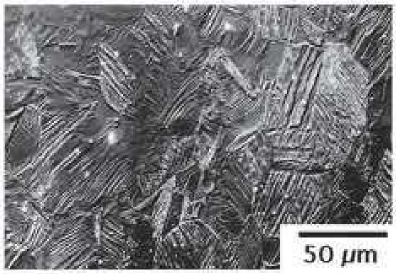
Ferritic-bainitic steels are designed for high strength flangeability and high hole expansion. Strengthening is mainly obtained by grain refinement. The can be obtained by hot rolling. FB steels have the strength of HSLA, but higher n and total elongation. Because of their good weldability, they are considered for tailored blank applications.

Twinning induced plasticity steels

Twinning induced plasticity steels (TWIP) have Manganese up to 25% to obtain a fully austenitic structure at room temperature. During plastic deformation, twinning occurs and causes a high value of n, the microstructure becomes finer as twin boundaries act like grain boundaries and strengthen the steel.



TWIP steels have very high elongation at break and UTS (over 1 GPa) thanks to a dynamic Hall-Petch effects: twins form during deformation, refining the structure. TWIP steels retain very high ductility down to -150 °C and high strain rate (toughness), because FCC austenite does not undergo ductile to brittle transition.



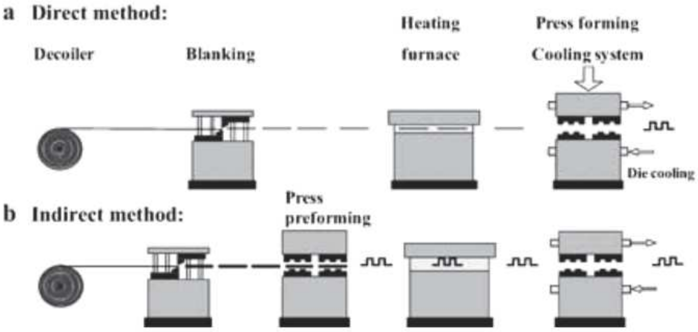
Hot formed steels

Hot formed steels are designed for press-hardening applications. The hot part is pressed and quenched to obtain complex shapes without springback.

Boron (0.001/0.005%) steels have very high hardenability.

A typical minimum temperature of 850 °C is held during forming, and a cooling rate greater than 50 °C/s. since quenching occurs in the press, lower cooling rates are achieved.

- Direct hot forming involves complete deformation at Taust, then quenching.
- Indirect hot forming involves preforming of the blank at room temperature, then press-hardening at Taust.



Post-forming heat-treatable steels

Post-forming heat-treatable steels are designed to maintain part geometry during and after heat treatment. Air hardening steels feature good forming properties in the soft state and high strength after heat treatment. This is crucial for large components and parts with great thickness.

Nanobainitic steels

NB steels feature acicular ferrite and retained austenite.

A nanostructured material contains large density of strong interfaces and small precipitates. Orowan mechanism postulates that a large number of small precipitates strengthens more than large precipitates. Grain boundaries and precipitates hinger dislocation movement.

It should be possible to make samples which are large in all dimensions, and they must be cheap to produce.

While AHSS were produced with interface distances in the order or 250-100 nm, nanobainitic steels have a structural scale one order of magnitude smaller.

Fine grained materials can be produced by introducing a large number of defects such as dislocations which interfere with slip or twinning. Defects can be introduced by deformation, and in this case Severe Plastic Deformation (SPD) is used.

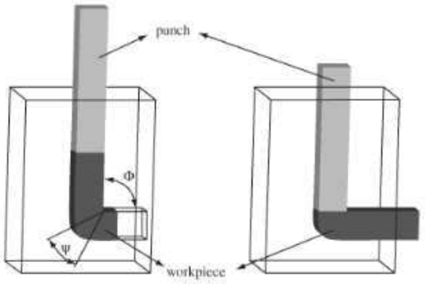


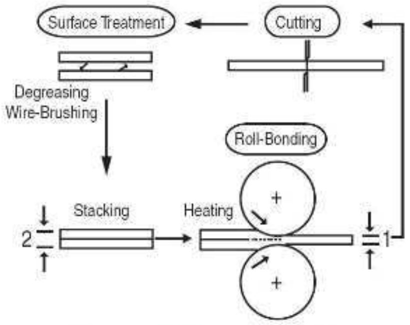
Figure 1. Illustration of the ECAP die geometry.

Equal-channel angular extrusion

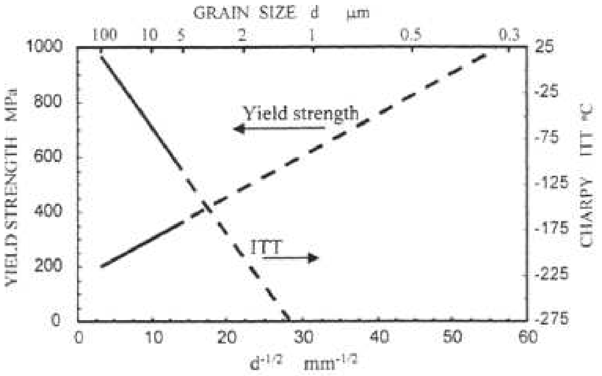
1) Equal-channel angular extrusion is a cold process to achieve large strains while maintaining the external shape.

2) Accumulative roll bonding involves rolling and folding of sheets to increase strain without thinning the sample entering the rolls

3) Thermomechanical processing involves the phase transformation from deformed parent austenite. The minimum ferrite grain size is 1 um.



Accumulative roll bonding

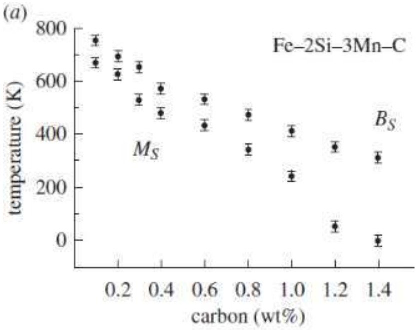


Ductility decreases sharply as the grain size decreases (impact transition temperature).

The larger the undercooling, the higher the nucleation rate and the lower growth rate: the transformation should occur at low temperature (about 250 °C) to allow the formation of a fine grain size.

It appears that there is no lower limit to the temperature at which bainite can form: Ms can be lowered by increasing carbon content, allowing bainite to form easily.

The kinetics of the process slows down as the temperature is reduced. For practical purposes, a transformation time of tens of days is reasonable.

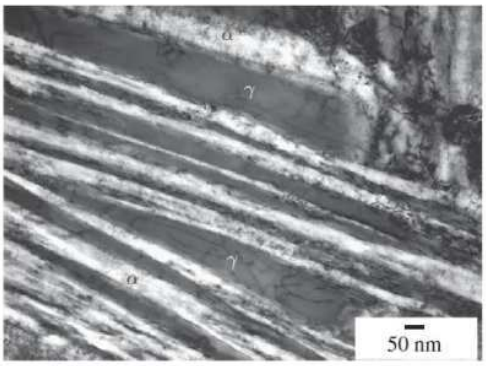


Microstructure: nanosized ferritic bainite plates (20-30 nm), stable austenite between plates, high density ferrite-austenite interfaces, no carbides.

Composition: silicon is used to delay carbide precipitation, so that $\gamma \rightarrow \alpha + Fe_3C$ becomes $\gamma \rightarrow \alpha_b + \gamma_{R,\ high\,\%C}$.

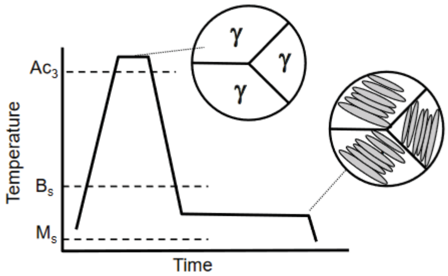
If the temperature overcomes a critical value,

$\alpha_b + \gamma_{C-rich} \rightarrow \alpha_b + Fe_3C$.



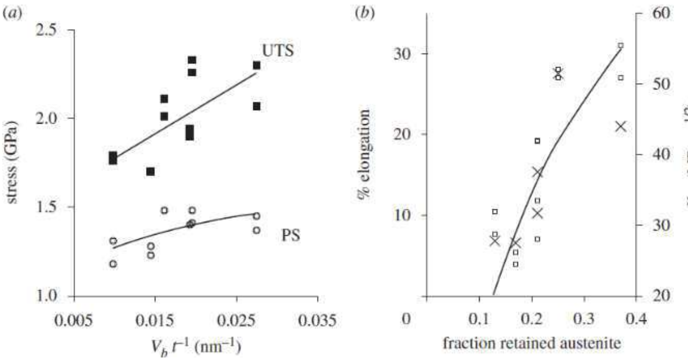
Strength comes from the thin platelets of bainitic ferrite. Ductility comes from the strain-induced martensitic transformation of retained austenite, enhancing work hardening capacity.

Since the transformation to nanobainitic steels occurs at relatively low temperatures (200-250 °C), substitutional atoms do not have time to diffuse. The only specie that partitions is carbon, rejected by bainitic ferrite as it forms, enriching retained austenite up to 5-7%. Nanostructure bainite is the hardest bainite ever achieved, reaching >700 HV.



Production process: austempering consists in austenitization above Ac3 (about 950 °C), transfer into an oven at lower temperature (200°C) for up to ten days, to allow bainite formation and prevent carbide formation.

Nanostructured bainite can be obtained even in large components because the tame taken to reach 200 °C is much less than that required to initiate bainite. Since cooling is slow, no residual stresses occur.



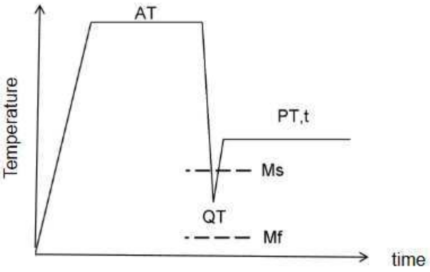
Yield stress and UTS increase by increasing bainite fraction and decreasing lamellar thickness. (Vb/r parameter). The toughness increases with the amount of retained austenite.

Strengthening contribution of carbon and dislocations are small in comparison with that due to plate size: this is why the hardness is insensitive to tempering until plate coarsening at 500 °C.

The addition of cobalt and aluminum boosts the driving force increasing the transformation rate.

Quenching and partitioning steels

Q&P is a heat treatment which produces a microstructure with ferrite and carbon-rich stabilized austenite. Austenite is partially quenched to martensite, then transformed from bct to bcc.

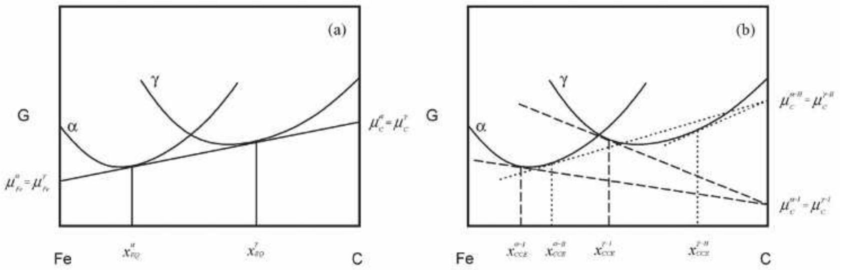


The heat treatment sequence involves:

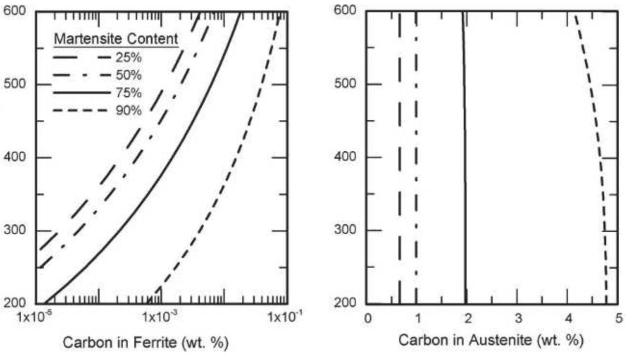
-quenching to a temperature between Ms, Mf, austenite → martensite + residual austenite. $\gamma \rightarrow \alpha' + \gamma_R$

-partitioning (typically above Ms) enriches the remaining austenite with carbon escaping from the supersaturated martensite, stabilizing austenite to room temperature: $\alpha' \rightarrow \alpha' \ (low\ C) + \gamma_r \ (high\ C)$

the model for carbon partitioning between martensite and austenite is the Constrained Carbon Equilibrium.



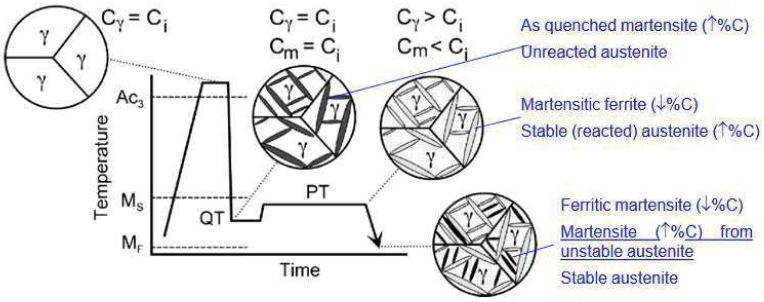
CCE model works under the hypothesis of large range diffusion of carbon with no partitioning of substitutional alloying elements. CCE is described by two conditions: the same chemical potential of carbon in ferrite and austenite, and the conservation of Fe and substitutional atoms in the two phases.



There are infinite alpha-gamma combinations satisfying the two conditions of CCE model.

The partitioning degree is determined by the fraction of the two phases after quenching, calculated with Koistinen-Marburger equation: $f = 1 - exp(Ms - T)$

Carbon in preferentially partitioned into austenite, which is stabilized and does not transform into martensite. Partitioning at temperatures around Ms yields low amounts of martensite and low %C in austenite; partitioning at about Mf leads to high %martensite and high %C in austenite.



The amount of carbon partitioning does not depend on the partitioning temperature, but only on quenching temperature ie. amount of martensite produced.

One would want higher partitioning temperatures to achieve faster kinetics, but the precipitation of transition carbides must be avoided, therefore lower temperatures are employed.

Austenite→martensite + retained austenite (after quenching) → ferrite + stable austenite (high %C)

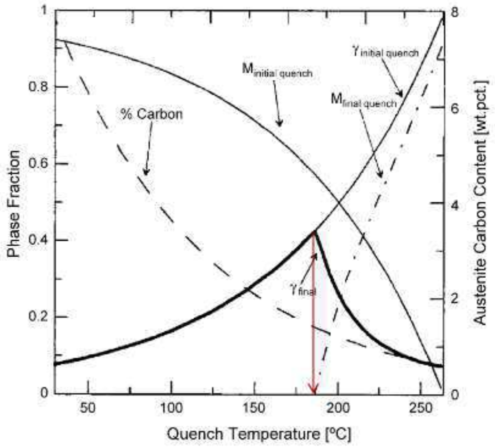
martensite + retained austenite → ferrite (low %C) + stable austenite (high %C) (after partitioning)

Carbon distribution in austenite is not perfectly homogeneous, so unstable austenite can transform into martensite which will be present in the final microstructure.

Above a certain quenching temperature, the austenite fraction in the final structure decreases again.

The optimum quenching temperature can be defined, at which the maximum content of stable austenite is reached, and no carbide precipitation of bainite formation occurs. At the OQT, the highest ductility is reached.

Increasing %C, Ms decreases and the fraction of austenite increases.

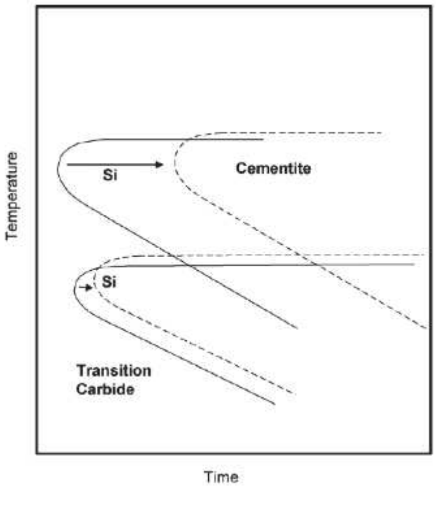


Experimental curves show lower amounts of retained austenite than those calculated from CCE: this is because competitive reactions such as carbides precipitation can occur.

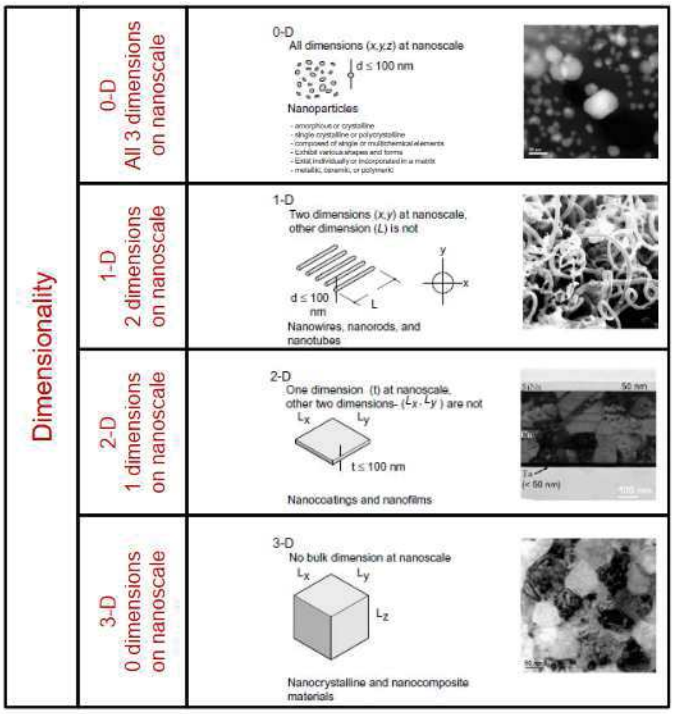
In steels with high Ms, precipitation of transition carbides can occur still during quenching, before partitioning, at very low temperatures. These steels are referred to as self-tempering.

Silicon is very efficient in delaying cementite precipitation due to its low solubility in Fe3C. transition carbides are stabilized by Si, and the precipitation is not delayed.

Partitioning temperatures close to 400 °C are preferred as the cementite precipitation is delayed and the precipitation of transition carbides is avoided.



Nanostructured metallic materials



Nanomaterials have at least one dimension in the nanoscale (1-100 nm).

Depending on the dimensions in which the size is at nanoscale, they can be classified into:

-nanoparticles, zero dimensionality ie. all dimensions on the nanoscale. These find applications in pharmaceuticals, cosmetics, electronics, optoelectronics (quantum dots) etc.

-layered or lamellar structures have only the thickness at nanoscale. These are used as thin films for electronic devices.

-filamentary structures as nanowires, nanorods and nanotubes have two dimensions at nanoscale

-bulk nanostructured materials consist of large materials made of nanosized crystallites or are amorphous materials.

The higher the dimensionality, the more complex the definition.

A material may be categorized as a nanomaterial simply on the basis of its internal structural dimensions, regardless of its exterior dimensions.

Lamellar structures on nanoscale can be nanocrystalline or microcrystalline: both are defined as nanomaterials. There are typically used as coating, not on their own.

In multilayered structures, each layer can be at nanoscale or above. These result in tougher materials because every layer can arrest facture, yielding very high fracture toughness.

The composition of multilayered nanocoatings can be tailored to reach maximum adhesion and mechanical properties. For example, a TiN coating (better adhesion) on steel with increasing Al composition until pure AlN is reached (higher hardness).

3D bulk nanomaterials exhibit features at the nanoscale such as grain size or precipitates. For example, nanobainitic steels have grain size at nanoscale, precipitation hardened alloys have precipitates at nanoscale.

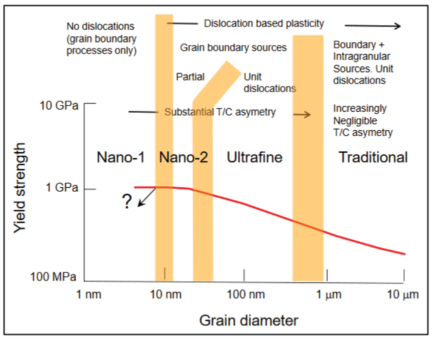
Nanocomposites are formed by two or more materials with very distinctive properties that act synergistically to create properties that cannot be achieved by single materials alone. They can either be composed of a matrix reinforced by nanoparticles, nanowires, nanotubes, or layered structures.

The properties reached can be higher than those predicted by rule of mixtures, but there are many problems related to defect from manufacturing.

Nanocomposites are very hard to sinter, and porosity represents an issue which can hardly be solved.

Being nanomaterials very hard, workability and machinability become very low, and processing becomes very expensive.

Severe plastic deformation can be used to clear the original microstructure and obtain nanoscale features. For example, gold foils can be beaten until nanometric thickness is reached.



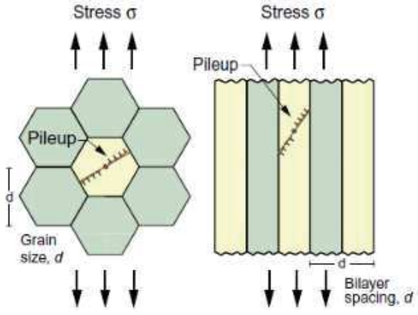
The original definition of nanomaterials is not always appropriate: it is better to refer to a specific size-dependent property that exhibits a critical dimension at nanoscale. For example, the ferromagnetic coercitive force has a critical size at the nanoscale.

The larger surface area/volume of nanomaterials plays an important role in dictating the properties of the material.

The Hall-Petch relationship stops working below about 50 nm. At normal grain size, dislocation movement is the mechanism that justify Hall-Petch relationship. At nanometric grain size, dislocations cannot pile up inside the grains, so dislocation slip is not the mechanism which governs the deformation. Grain boundary sliding is the possible mechanism below a certain grain size.

Ultrafine grain size (100-500 nm) materials show interesting properties and are easier to obtain than nanomaterials.

Hardness increases as the grain size decreases since it is related to the strength of the material.

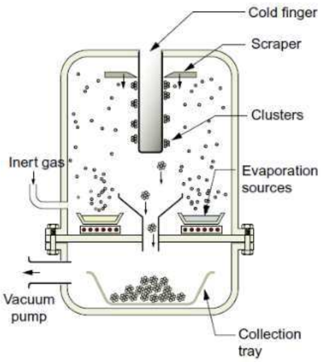


For normal materials, strength is measured by the force f* per unit length of dislocation required to cut through the boundary and trigger the slip in the next grain. The number of dislocations in a pileup scales with the applied stress and the distance between dislocation source and obstacle.

The smaller the grain size, the lower the number of dislocations N which can pile up. When N falls to 1, no pileup is possible.

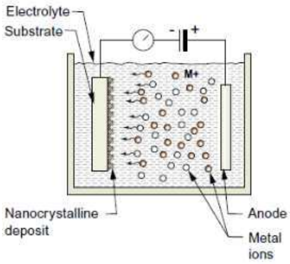
Different processing techniques are employed to produced particles, wires, tubes, films or bulk forms.

- Inert gas condensation: feed is let evaporate, condensates in a cold finger and falls down to a collector. Once the atoms boil off, they quickly lose their energy by colliding with the inert gas. The vapor cools rapidly and supersaturates to form nanoparticles that collect on a finger cooled by liquid nitrogen. The particles are harvested by scraping them off the finger and are collected, still protected by the inert gas. As particles form they tend to cluster and increase their size.

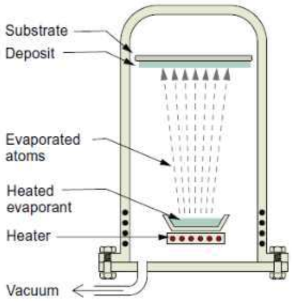


- Sol-gel deposition: a solution of inorganic salts or metal-organic compounds such as alkoxides are polymerized to form a colloidal suspension (sol). The particles are kept in suspension by adding a surfactant. The suspension can be treated to extract the particles for further processing or cast onto a substrate. Then it is converted to a gel by chemical treatment to disable the surfactant to create an extended network of connected particles. Evaporation of the solvent then leaves a dense or nanoporous film.

- Pulsed electrodeposition: crystal growth is stopped by pulsing the voltage and adding growth inhibitors that condense on crystal surfaces during the off phase of the pulse. This technique can yield porosity-free nanocrystalline deposits as thick as 5 mm that require no further processing. Edge effect is a problem in this technique as a stronger electric field at the corners.

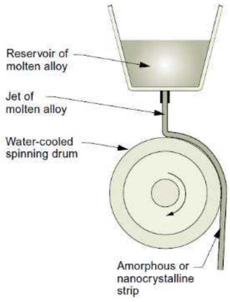


- PVD: vapor is created in a vacuum chamber by direct heating or electron beam heating of the metal, from which it condenses onto the cold substrate. By introducing a reactive gas, compounds can be formed (eg. Sputtering Ti in a nitrogen atmosphere, giving TiN). Three variants are distinguished:
plating, with no potential difference between bath and workpiece;
ion plating, the workpiece is the cathode and the source is the anode, so the vapor is accelerated by an electric field;
sputtering: Ar ions are accelerated onto a target, ejecting ions onto the component surface.

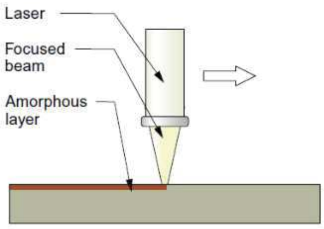


- CVD is similar to PVD, but the reactants are introduced in a vacuum chamber, and the product of the reaction precipitates onto the substrate.

PVD involves temperatures up to 500 °C, whereas CVD requires higher temperatures, up to 900 °C.

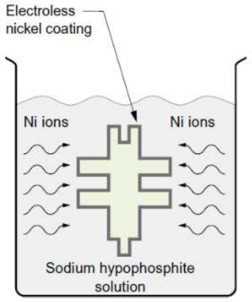


- Melt spinning consists in casting molten metal onto a rotating wheel, yielding cooling rates up to 10^7 °C/s, giving amorphous or nanocrystalline wires or ribbons.
- Laser surface hardening consists in melting down a very thin layer of a bulk material, and cooling by conduction is very fast.
- Equal channel angular extrusion is the most diffuse severe plastic deformation technique, yielding grain size in the range 200-300 nm. The resulting parts are very hard and have to worked by electro discharge machining (EDM).



The major methods of severe plastic deformation are severe plastic torsion straining under high pressure (HPT) and equal channel angular pressing (ECAP)

- Electroless deposition involves no electric current. Electroless nickel deposits spontaneously onto almost anything plunged into a bath containing nickel ions and a reducing agent. The deposit is very hard, resistant to wear and corrosion, and most importantly cheap.



All powder consolidation processes involve applied pressure. Deformation processes having significant shear stress components are desired:

Extrusion: powders inside a container and pushed through a die

Sinter forging: pressure applied in a hot mold

Uniaxial hot pressing

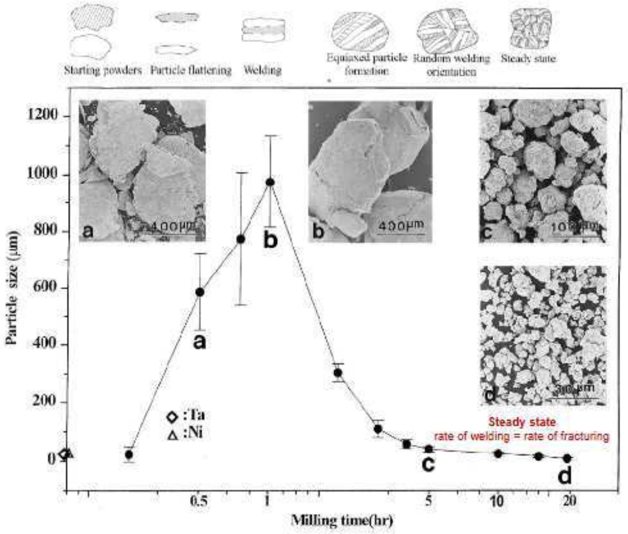
Hot isostatic pressure: hydrostatic pressure is provided by a gas or a liquid.

The ball milling of powders can be divided into two categories:

-mechanical milling of elemental or compound powders

-mechanical alloying of dissimilar powders in which material transfer occurs.

The minimum grain size obtainable by milling has been attributed to a balance between the defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes.



Particles are spun in a high energy ball mill. The particles flatten, weld and then break up. The process creates heavily deformed mechanically alloyed particles with a nanoscale internal structure. Filling the mill with inert gas promotes welding; cryomilling prevents coarsening of the structure.

The particles are subsequently compacter and sintered to make the final product.

In homogeneous mixing between different powders, the particle size reaches a steady state after a certain milling time.

Mechanical alloying is very efficient thanks to the contributions of SPD, temperature and microstructure.

SPD produces crystal defects so that the diffusivity of solute elements into the matrix is enhanced.

Temperature rise increases diffusivity (Arrhenius-like law).

Microstructure refinement decreases diffusion distances.

Type of mill, container, speed, time, grinding medium, ball-to-powder ratio, filling, atmosphere, process control agent, milling temperature are the main parameters influencing the process.

Sintering of metallic powders yields UFG materials.

Three major limitations to ductility for nanocrystalline materials can be identified:

- Artifacts from processing
- Force instability in tension
- Crack nucleation or propagation instability

For most metals with grain sizes below 50 nm the strain at break values are very low (<2-3%).

The smaller the grain size, the fewer the dislocation that can be packed into a pileup.

Strain hardening is needed in order to minimize mechanical instabilities that lead to local deformation and failure. The ability to strain harden becomes an important criterion for ductility in nanostructured materials.

An approach that has been used to provide strain hardening in nanostructured materials is to introduce a bimodal grain size distribution by appropriate processing methods.

The supposition was that larger grains should deform by the usual dislocation mechanisms and provide strain hardening, while the smaller nanoscale grains would provide the strength and hardness.

This harmonic structure is achieved by powder metallurgy. Mechanical milling induces deformation to the particles, yielding a coarse grained core and a fine grained shell. When these particles are sintered, the result is a continuous nanograined matrix with islands of coarse grained material.

The larger grains deform by the usual dislocation mechanisms and provide strain hardening, whereas the smaller nanoscale grains provide strength and hardness.

The intrinsic moduli of nanocrystalline materials are essentially the same as those for conventional grain size materials, until the grain size becomes very small (below 5 nm), such that the number of atoms associated with the gain boundaries and triple junctions become very large.

Fracture toughness is very important for high strength materials. The critical crack length $a_T = \frac{K_{IC}^2}{\pi\sigma_y^2}$ delineates the linear elastic from the elastoplastic fracture mechanics regime.

For defect sizes or crack lengths larger than 2-3 times a_T, the fracture strength is controlled by the fracture toughness and the crack length.

Only for defects smaller than a_T the fracture stress is solely governed by the strength of the material. For high strength materials, the transition length becomes significantly smaller.

In the regime of elastoplastic fracture mechanics, the fracture sstrain is governed by fracture toughness and yield stress. The fracture strain is $\epsilon_f = \frac{K_{IC}^2}{aE\sigma_y}$

An important feature of SPD-processed materials is a pronounced alignment and elongation of the microstructure into the principal deformation direction, yielding fracture toughness anisotropicity.

In coarse grained metals, two main mechanisms control the fracture toughness: micro-ductile crack propagation, crack propagation by de-cohesion.

In nanocrystalline materials, the mechanisms are similar but intergranular fracture prevails and de-cohesion occurs by cleavage grains.

There is no sufficient space to form the necessary dislocation pile-ups or there are always sufficient boundaries where de-cohesion is easier than the cleavage of the grains.

Microductile crack propagation: tendency to crack branching into the crack propagation direction parallel to the grain elongation. The critical crack tip opening displacement, before the coalescence of the blunted crack tip with the micro and nano-pores takes place, is between a few and 100x grain size.

Brittle crack propagation: crack propagates by grain boundary decohesion with intergranular fracture when the crack propagation direction is parallel to the aligned grains. The fracture toughness for this loading direction is relatively small.

Metallic Matrix Composites

All MMCs have a metal or a metallic alloy as the matrix. The reinforcement can be metallic or ceramic. Depending on the type of reinforcement, one can distinguish:

- Particle reinforced MMC
- Short fiber or whisker reinforced MMC
- Continuous fiber or sheet reinforced MMC
- Laminated or layered MMC

Particle reinforced MMC have assumed special importance for a different reasons: they are inexpensive, can be processed by casting or powder metallurgy, allow for high temperature use, increase stiffness, strength, thermal stability, wear resistance, and are relatively isotropic compared to fiber reinforced composites.

Metal casting route is cheaper than powder metallurgy.

Liquid-phase processes allow for near net shape, faster rate of processing.

There are four main liquid-phase processing techniques:

- Casting or liquid infiltration
- Squeeze casting or pressure infiltration
- Spray co-deposition
- In situ processes

In conventional casting, the particles and matrix mixture are cast into ingots and secondary mechanical processing, such as extrusion or rolling, is applied to the composite.

Alloys with low reactivity with the reinforcement should be used, to avoid the formation of undesirable compounds.

Stirring of the melt prevents sinking of the heavier reinforcement particles and ensures homogeneity.

Centrifugal casting allows for the optimal placement of the reinforcement by inducing a centrifugal force during casting to obtain a gradient in reinforcement volume fraction.

The reinforcement is intentionally segregated to improve the performance of the most critical region of the section.

Pressureless liquid infiltration is a process by which a particulate filler is infiltrated with pure Al or Al-Mg alloy. The temperature is typically around 700-800 °C for pure Al, 700-1000°C for Al-Mg, and the process is conducted in N2 atmosphere to minimize interfacial reactions.
Typical infiltration rates are less than 25 cm/h.

Squeeze casting involves forcing the liquid metal matrix into a short fiber or particulate preform. This involves shorter processing times and makes it possible to produce more complex shapes. The short processing time minimizes the interfacial reaction between reinforcement and matrix.
Minimal residual porosity and shrinkage are observed due to the applied pressure are obtained.
Both short fiber or continuous fiber reinforced composites can be produced with this technique, with a relatively high reinforcement volume fraction.

Spray co-deposition is used to fabricate metallic alloys in powder form. The metal or alloy is melted and atomized with water or an inert gas. Rapid solidification of thee liquid takes place, resulting in a fine solid powder. This technique can be modified by injecting reinforcement particles or co-depositing the particles with the matrix alloy.
The equipment is very expensive, but it produces at a very high rate (6-10 kg/min) and thanks to the very fast solidification rate, reactions between matrix and reinforcement are minimized.

In the reactive in situ processes, two components are allowed to react exothermically to form the reinforcement phase. The matrix consists of Al, Ni, or an intermetallic. The number of composite systems where reaction processing is beneficial is limited
The advantage of in situ reactions is that the reaction eliminates problems typically associated with wetting of the particle, so a relatively clean and strong interface is typically formed.
Nonreactive in situ processes take advantage of two phase systems, such as eutectic or monotectic alloys to form the fiber and matrix. Controlled directional solidification is used to separate the two phases in the right microstructure. Induction heating and crucible cooling are used to control the system. The fineness of the microstructure can be controlled by controlling the solidification rate.

Powder metallurgy is the most common solid-phase process. Discontinuous reinforcements (particles, short fibers) are easy to mix and blend. The composite mix is then isostatically cold compacted and hot pressed to full density. The fully dense compact then typically undergoes a secondary operation such as extrusion or forging.

One of the problems with bonding metallic powder particles is the oxide skin on the particle surface, in particular in Al. Degassing and hot pressing in an inert atmosphere contribute to the removal of Al hydrides, making the oxide skin more brittle and thus more easily sheared.
The ratio of reinforcement to matrix particle size is very important in achieving a homogeneous distribution of particles in the matrix: with larger matrix particle size, the reinforcement is pushed and packed in the interstices. A particle size ratio closer to 1 yields a more homogenenous microstructure.
Particle clustering can be quiantified by measuring the nearest-neighbor distance of each particle. The coefficient of variance of the mean near-neighbor distance is used: $COV_d = \frac{\sigma_d}{d}$

Extrusion is a secondary deformation processing of MMCs. The shear yields the fracture of the oxide skin in Al particles, enhancing bonding between particle and matrix. It is mainly used to consolidate composites with discontinuous reinforcement, yielding an alignment of particles along the extrusion axis.

Forging is a secondary deformation processing primarily used to consolidate composites with discontinuous reinforcement, to minimize reinforcement fracture.
In sinter-forging a mixture of reinforcement and matrix powders is cold compacted, sintered and forged nearly to full density.

Pressing and sintering is relatively inexpensive and simple. Composite powder systems are typically sintered at a temperature range to obtain some degree of liquid phase. The liquid phase flows through the pores in the compact, resulting in densification of the composite.
Other techniques: roll bonding to produce laminated composites, co-extrusion to insert superconductor wires in a copper matrix.

The extent of contact between a liquid and a solid is described by the wettability. The wettability is the ability of a liquid to spread on a solid surface.
Thermodynamically, spreading of the liquid will occur if this results in a decrease in the free energy of the system: $\gamma_{SL} + \gamma_{LV} \cos\theta = \gamma_{SV}$
Low contact angle yields good wettability, necessary but not sufficient for strong bonding.
The bonding at the interface can be either chemical or mechanical.

The behavior of MMCs depends on several factors:

- reinforcement volume fraction,
- particle size,
- particle shape
- matrix microstructure.

- Increasing the reinforcement volume fraction, the stiffness increases, strength increases, ductility decreases. The lower ductility is attributed to the earlier onset of void nucleation with increasing reinforcement, and the high stress concentration at the tips of the cracked particles. Toughness decreases with increasing volume fraction of reinforcement (stress triaxiality).
- Increasing the particle size, the strength decreases, work-hardening rate decreases, ductility decreases (nucleated voids coalesce more easily). For a given volume fraction of reinforcement, the toughness of the composite decreases slightly with decreasing particle size.

It the strength of the interface is greater than the particle strength the particles fracture before the interface; is the strength of the interface is less than the particle strength, void nucleation and growth will take place at the interface.

The ductility of the composite is also a function of the degree of particle clustering.

With increasing clustering, the toughness decreases.