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MILANO 1863

SCHOOL OF INDUSTRIAL AND INFORMATION ENGINEERING

MATERIALS ENGINEERING AND NANOTECHNOLOGY

Metallic materials and Product innovation

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Academic Year 2023–2024

Author's preface

Dear Reader,

I am delighted to present this comprehensive collection of lecture notes for ‘**Metallic materials and Product innovation**’. These notes have been thoughtfully structured to closely align with the course curriculum, providing an invaluable resource for your studies.



These lecture notes are a culmination of extensive research and diligent note-taking, incorporating insights from professor lectures, course materials, textbooks, and other reputable sources. By bringing together these diverse resources, I aimed to provide you with a well-rounded understanding of the subject matter.

While every effort has been made to ensure accuracy and clarity, it is essential to acknowledge that errors or discrepancies may exist within these notes. The complexities inherent in the subject matter, coupled with the limitations of human interpretation, make occasional inaccuracies unavoidable. Therefore, I encourage you to approach these notes critically, supplementing your understanding with additional academic sources and seeking clarification from your professors or peers when necessary.

I have written these lecture notes using L^AT_EX, a precise typesetting system widely used in scientific and academic writing. Its utilization ensures a visually appealing and organized document, enhancing the overall readability and accessibility of the content.

I sincerely hope that these lecture notes will serve as a valuable companion throughout your academic journey. They are designed to supplement your learning experience, providing a comprehensive overview of the course material. Remember to approach these notes as a guide, actively engaging in discussions, seeking further insights and embracing the collaborative spirit of academia.

Wishing you success and an enriching learning experience.

 Milano, Italy
 February 13, 2026

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1 Shape Memory Alloys

Shape Memory Alloys (SMAs) are a class of metallic materials that exhibit a reversible solid-state phase transformation between two distinct crystal structure at specific temperature ranges.

This transformation results in the remarkable ability of SMAs to return to a predefined shape or configuration when subjected to thermal or mechanical loading and unloading cycles.

SMAs are functional materials that show two peculiar properties^[1]:

- **Shape Memory Effect (SME)** → When subjected to an increase in temperature beyond their A_f temperature, SMAs will revert to their original, undeformed austenite phase shape, exhibiting the shape memory effect. This transformation is entirely reversible and can be repeated multiple times.
- **Pseudoelasticity/Superelasticity** → SMAs also exhibit a superelastic behavior within a certain temperature range, allowing them to undergo substantial reversible deformation without permanent damage, known as the “pseudoelastic” or “superelastic” effect.

Both those effects are based on a **martensitic transformation**.

1.1 Martensitic transformation

Martensitic transformation

The **martensitic transformation** is a shear-dominant diffusionless solid-state phase transformation that occurs in certain materials, such as SMAs, and is characterized by a change in crystal structure from one phase to another.

Specifically, it involves the transformation from the austenite phase to the martensite phase or vice versa, occurring by nucleation and growth of the phase. This transformation can be triggered by changes in temperature, stress, or a combination of both.

The martensitic transformation is associated with an inelastic deformation of the crystal lattice with NO diffusive process involved. Austenite and Martensite phases coexist during the phase transformation (first order transition) and, as a result, there exists an invariant plane, which separates the parent and product phases.

Note

A **diffusive process**, often referred to simply as diffusion, is a fundamental physical phenomenon in which particles, atoms, molecules, or other entities move from regions of high concentration to regions of low concentration. This movement occurs due to random thermal motion, with particles tending to spread out and mix over time until they are evenly distributed throughout the available space. Diffusion is driven by the natural tendency of particles to seek a state of higher entropy, which corresponds to a more uniform distribution.

This transformation is **crystallographically reversible**.

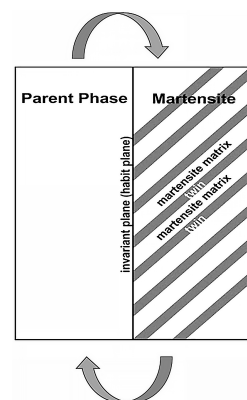


Figure 1: Martensitic Transformation

^[1]Further information will be addressed later.

Since the crystal lattice of the martensitic phase has lower symmetry than that of the parent austenitic phase, several variants of martensite can be formed from the same parent phase crystal.

Martensite can undergo transformation in two primary ways: **Thermally Induced Martensite (TIM)** and **Stress Induced Martensite (SIM)**.

1.1.1 Diffusive transformations

Diffusive transformation

A **diffusive transformation**, often simply referred as “diffusion-driven transformation”, is a phase transformation in a material that occurs as a result of the movement of atoms or molecules within the material.

Unlike martensitic transformations, which involve a change in crystal structure, diffusive transformations primarily involve the rearrangement of atoms within the existing crystal structure of the material. These transformations typically occur over longer periods of time and are driven by the diffusion of atoms through the material.

The key aspects of this transformation are:

- Formation of a phase with a new chemical composition
- They occur thanks to the transport of atoms over relative distances
- Diffusion of atoms takes time to take place (time dependent)
- They can be suppressed by quenching^[2] because the transformation is going to be suppressed/freeze from the process
- They are defined as isothermal because they can proceed over time at a constant temperature

1.1.2 Displacive transformations

Diffusionless transformation

A **diffusionless transformation**, also known as a displacive transformation or a diffusionless solid-state transformation, is a phase transformation in a material that occurs WITHOUT the diffusion of atoms or ions through the material. Unlike diffusive transformations, which involve the movement of particles and atoms to form a new phase, diffusionless transformations involve abrupt changes in the arrangement of atoms without significant atomic migration.

The key aspects of this transformation are:

- They do NOT modify the composition of the parent phase, but only the crystalline structure
- Atoms rearrange themselves in short-range cooperative motion
- Since no atomic migration is necessary, displacive transformations progress almost independently of time, with the speed of the interface between two phases, able to move at the speed of sound

^[2] **Quenching** is a heat treatment process to rapidly cool a material, typically a metal or alloy, from a high-temperature state to a much lower temperature. The primary purpose of quenching is to achieve specific material properties or to lock in a particular microstructure within the material.

- They are referred to as **athermal transformations** [?], since they do not progress at a constant temperature and the amount of the new phases present depends only on temperature, not time
- Martensitic transformations are **displacive transformations**. The term “martensite” refers to the stable phase at low temperature and austenite refers to the stable parent phase at high temperature.

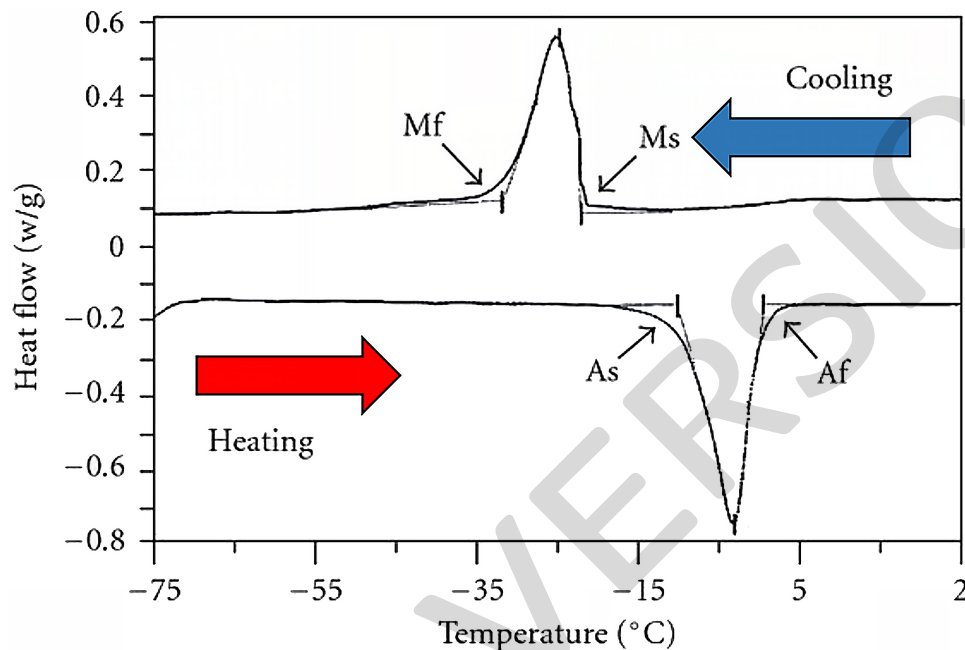


Figure 2: Characteristic Temperature of the Martensitic Transformation

In the Figure 2 it is possible to identify 4 different temperature values:

- **Martensite Start (Ms)** → is the highest temperature at which austenite begins to transform into martensite as the material is cooled. Below this temperature, no martensitic transformation occurs
- **Martensite Finish (Mf)** → is the temperature at which the martensitic transformation is considered complete during cooling. Below the Mf temperature, the material is fully in the martensite phase
- **Austenite Start (As)** → is the temperature at which austenite begins to reappear during heating after the martensitic transformation has taken place. It signifies the end of the martensitic phase
- **Austenite Finish (Af)** → is the highest temperature at which martensite transforms back into austenite as the material is heated. Above this temperature, the material is fully in the austenite phase

Note

These characteristic temperatures are specific to the material and its composition. The values of Ms, Mf, As, and Af can vary widely among different shape memory alloys and steels, and they are determined by factors such as alloy composition, microstructure, and processing conditions.

It's evident that the martensite and austenite transformations vary in terms of the temperature at which they take place. The integral of the curve represents the enthalpy of the transformation,

essentially indicating the heat released or absorbed during the process.

The Martensitic Transformation in SMAs takes place through two distinct contributions:

- **Bain deformation** (Lattice deformation) → This deformation consists of all the atomic movements that serve to produce the new crystalline structure: very small atomic shifts are required to advance the interface (see Figure 3).
Bain deformation is commonly observed in materials with cubic crystal symmetry, such as face-centered cubic (FCC) or body-centered cubic (BCC) structures. It often involves a transformation from one cubic form to another by shearing^[3].

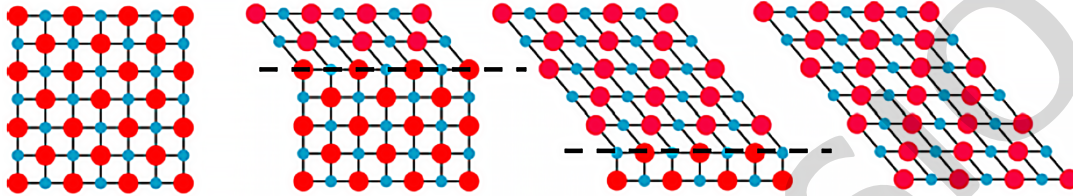


Figure 3: Bain deformation

- **Lattice-invariant shear** (Laves shear) → This shear deformation is characterized by the sliding or shearing of atomic planes within the crystal structure while preserving the overall symmetry and lattice parameters of the crystal. Thus, there is an accommodation of the shape variation that allows the new martensitic phase to stay within the austenitic matrix that surrounds it (see Figure 4).

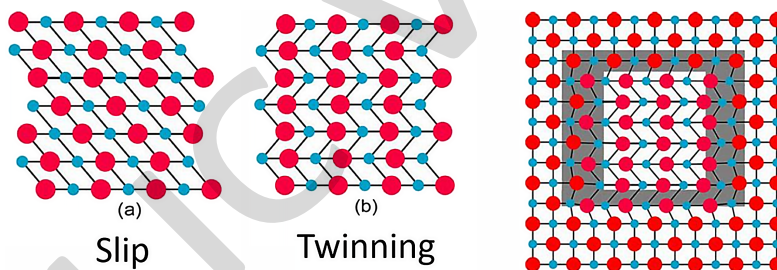


Figure 4: Lattice invariant shear

This accommodation can occur through the phenomenon of sliding dislocations (slip) as in steels or through the formation of twinning as occurs in many SMAs.

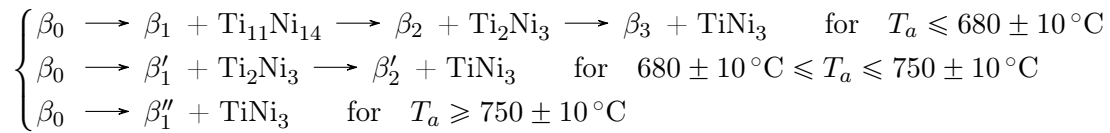
During martensitic transformation, the crystalline lattice undergoes a shearing parallel to a particular crystallographic plane. The different potential orientations in which such shearing can be produced are named “**variants**”.

1.2 Slip

Slip and **Twinning** are two distinct mechanisms of plastic deformation in crystalline materials. They both involve the **movement of atoms or planes** within a crystal lattice but operate differently and result in different types of crystallographic changes.

The main characteristics of the slip are:

^[3]**Shearing** is a mechanical deformation process in which parallel planes within a material shift or slide past one another. This type of deformation results in a change in the shape of the material without altering its volume.



1.9.6 Effect of alloying elements

90% of applications containing SMAs use binary NiTi with a Ni content between 49 and 51% at. without further alloying elements.

Interstitial atoms, such as carbon and oxygen, are present in very low quantities (few hundreds of ppm) and are considered as impurities to be eliminated.

For particular application, substitutional elements are used (NiTiX e.g. NiTiFe, NiTiNb, NiTiCr, NiTiCu, NiTiCo, NiTiV, NiTiPt and NiTiHf) to control the functional properties:

- Increase the hysteresis: Nb
- Reduce hysteresis: Cu
- Increase transformation temperature: Pt, Pd, Hf, Zr
- Reduce transformation temperature (or increase the stiffness of B2): Fe, Co, V, Cr, Mn, Al, Ta
- Increase radiopacity: RE
- Increase mechanical strength, corrosion resistance or creep: Ti, Al

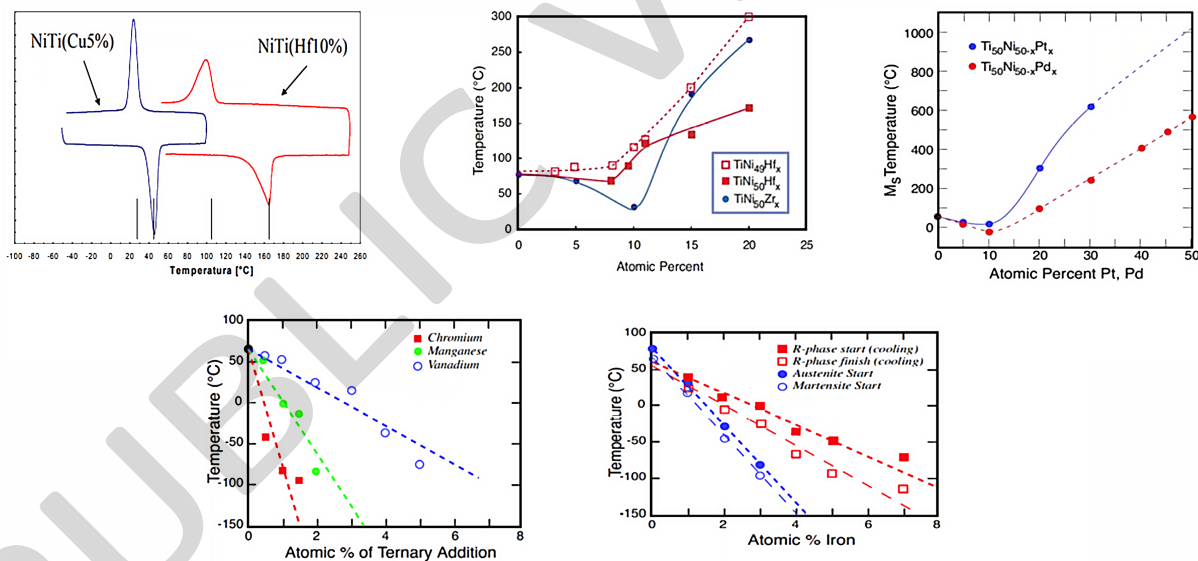


Figure 18: Effect of Alloying elements

1.9.7 Effect of Oxygen

The presence of **oxygen** in SMAs can have both positive and negative effects, depending on the context and specific applications:

- **Oxidation:**
Oxygen can react with the alloy's constituent elements, particularly with the nickel component: this can lead to the formation of an oxide layer on the surface of the SMAs (TiO_2 rutile), within the metal matrix ($\text{Ti}_4\text{Ni}_2\text{O}_x$) or with interstitial oxygen in NiTi lattice.

This process is often undesirable as it can compromise the material's mechanical properties, corrosion resistance and functionality. To mitigate this, SMAs are typically stored in controlled environments, such as vacuum-sealed packaging or inert gases.

- **Improved biocompatibility:**

In medical applications, controlled oxidation can be beneficial. The formation of a stable and biocompatible oxide layer can enhance their biocompatibility

- **Environmental considerations:**

Oxygen levels in the environment can impact the long-term stability and performance of SMAs. In applications exposed to varying oxygen levels, such as aerospace or outdoor applications, engineers must consider potential aging effect and degradation over time.

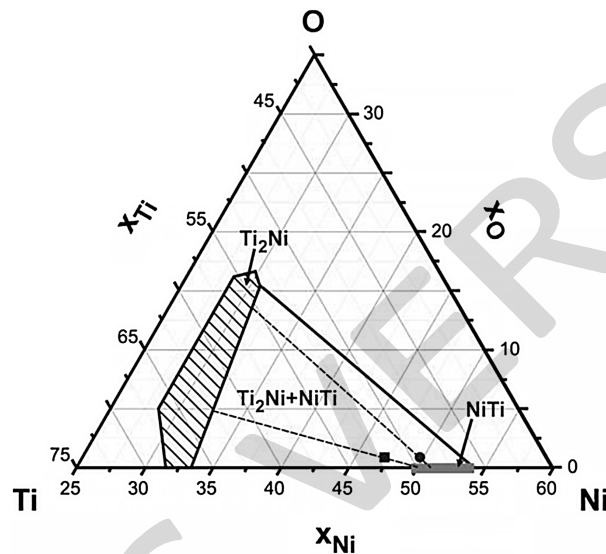


Figure 19: Effect of oxygen

Oxygen CANNOT be avoided (present in raw materials, especially Titanium, with 200–500 ppm). Oxygen has a higher solubility in Ti_2Ni than in $NiTi$; the Ti_2Ni precipitates can absorb oxygen until they reach the Ti_4Ni_2O composition.

$Ti_4Ni_2O_x$ compounds ($0 < X < 1$) are insoluble inclusions in the matrix and inert to heat treatment.

They can affect the fatigue resistance of the material. They are also present in alloys rich in Ni (superelastic). These Ti-rich inclusions modify the stoichiometry of the alloy, this lowering the transformation temperatures.

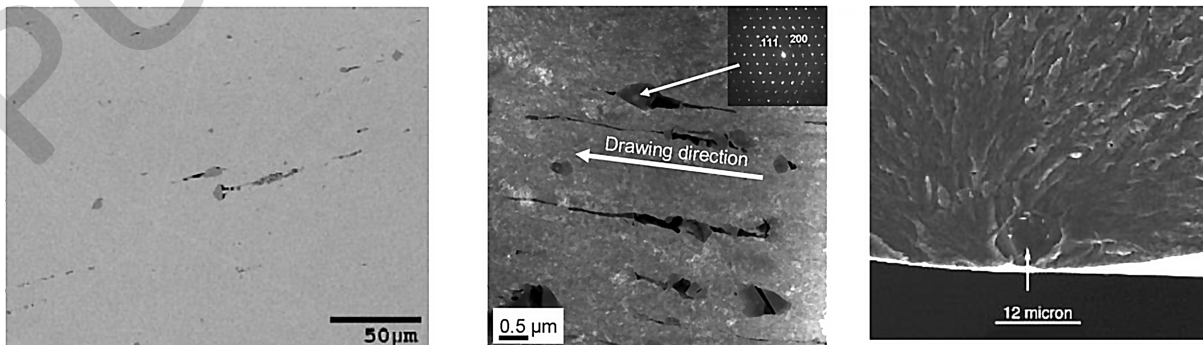


Figure 20: Effect of oxygen

1.9.8 Effect of Carbon

Carbon does NOT dissolve in NiTi, it forms carbides with Titanium (TiC). C is usually not present in the starting materials (Ti and Ni), it is introduced into the alloy only if the alloy is melted in a graphite crucible. Ti and Ni absorb C in the liquid phase; about half of the nitinol is produced in copper crucibles, so it does NOT contain C.

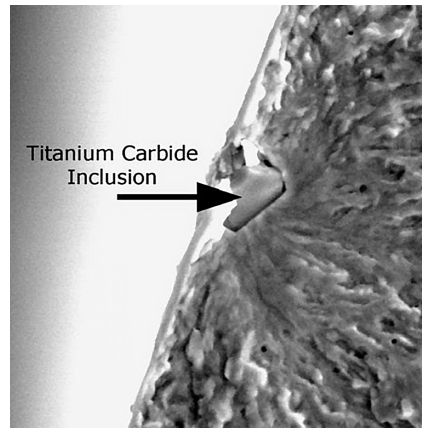


Figure 21: Formation of TiC

Note

TiC particles are generally micrometric in size and have geometric shapes with sharp edges; they can affect the fatigue resistance of the material.

To form TiC, the matrix is depleted in Ti, so the alloy composition needs to be slightly corrected.

1.10 Vacuum Induction Melting - VIM

Vacuum Induction Melting (VIM) [?] is an advanced metallurgical process used to the production of high-quality, high-purity alloys and metals. It involves melting and refining metal under vacuum condition to minimize contamination and achieve precise control over the alloy composition.

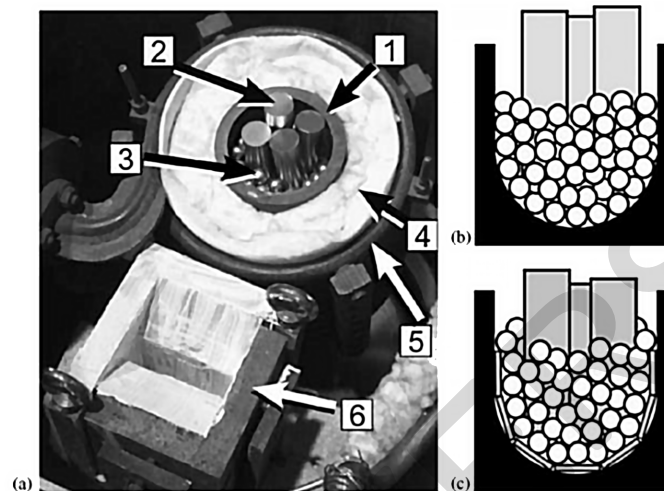
The key process involve the following steps:

1. **Vacuum Chamber:** The process begins inside a vacuum chamber, which is a sealed vessel designed to maintain a high vacuum. The vacuum environment prevents the metal from reacting with gases in the atmosphere and reduces the risk of contamination. Starting materials are Ni and Ti with high purity.
2. **Induction Heating:** An induction heating system is used to generate intense electromagnetic fields. An induction coil surrounds the graphite crucible or a water-cooled copper crucible itself.
3. **Melting:** The metal to be melted is placed in a crucible inside the vacuum chamber. When the induction coil generates an alternating magnetic field, it induces electrical currents within the metal. These currents produce heat through resistive heating, causing the metal to melt.
4. **Refining:** As the metal melts, any impurities or gases present are vaporized or removed through evaporation. This process helps to refine the metal, eliminating contaminants and

achieving a high-purity end product.

5. **Precise Alloying:** VIM allows for precise control over the alloy composition. Additional alloying elements can be added as needed to achieve the desired alloy composition.
6. **Casting:** Once the metal is fully melted, it can be cast into various forms (ingots, billets, custom shapes), depending on the specific application

The main drawback concerns the **high quantity of carbon impurities**: 300 – 700 ppm.



(a) Photograph of the graphite crucible with Ti-rods and Ni-pellets (1, graphite crucible; 2, Ti-rods; 3, Ni-pellets; 4, isolation; 5, water cooled copper coil; 6, mould); (b) schematic illustration of crucible filling: Ni-pellets are in contact with the crucible graphite and Ti-rods stick in the Ni-pellets; (c) same as in (b), but a Ti-disk cladding prevents direct contact between Ni and graphite

Figure 22: Vacuum Induction Melting

1.11 Vacuum Arc Remelting - VAR

Vacuum Arc Remelting (VAR) is a specialized metallurgical process used for refining and purifying high-quality alloys, particularly superalloys and specialty steel. It is an extension^a of the Vacuum Induction Melting (VIM) process and is employed to further enhance the purity and uniformity of materials.

^aOften, VIM and VAR are combined.

The key process involve the following steps:

1. **Vacuum Chamber:** The VAR process takes place inside a vacuum chamber, just like VIM. This vacuum environment prevents the molten metal from reacting with gases in the atmosphere, reducing contamination. Typically, a water-cooled copper crucible is used.
2. **Electrodes:** VAR involves two consumable electrodes—an electrode made of the metal to be remelted and a water-cooled copper electrode. These electrodes are positioned facing each other within the vacuum chamber. In particular, Ni and Ti are weighed in the right ratio and pressed together to form the consumable electrode of the VAR.
3. **Arc Discharge:** An electrical arc is initiated between the metal electrode and the copper

electrode. This arc generates intense heat, causing the metal electrode to melt. The copper electrode remains solid and acts as a heat sink.

4. **Melting and Refining:** As the metal electrode melts, impurities and contaminants are vaporized or driven out of the molten metal due to the high temperatures and vacuum conditions. This process further refines the material.
5. **Solidification:** After refining, the molten metal is slowly solidified as it moves upward from the bottom electrode to the top electrode. Controlled solidification rates are crucial to achieving the desired microstructure and properties.
6. **Continuous Casting:** In some VAR setups, the solidified metal may be continuously cast into a specific shape, such as an ingot or bar, as it rises through the chamber. This continuous casting can be customized to meet the requirements of various applications.

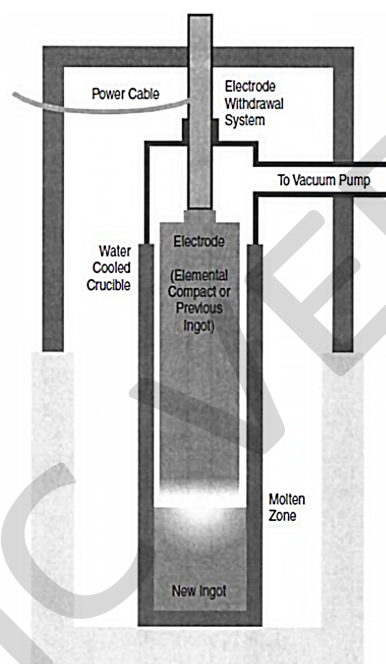


Figure 23: Vacuum Arc Remelting

The main advantages are the **high purity** and the **absence of carbon**; the main drawback is the **poor chemical homogeneity** of the ingot, which has to be remelted several times.

1.12 Shape settings

The term “**shape setting**” refers to the process of programming or establishing a specific shape in the material that it can “remember” and return to when subjected to the appropriate conditions.

Here’s how shape setting works:

1. **Programming the Initial Step:** Shape setting begins with the SMAs in its high-temperature austenitic phase, which is the phase with the desired shape. The SMAs is mechanically deformed or shaped into the desired configuration at an elevated temperature (above A_f); the material is held in this deformed state as it cools down to room temperature.

6 Metal Matrix nano-Composites

Metal Matrix nano-Composites (MMNCs) are a type of advanced material where a metal matrix is reinforced with nanoscale particles or fibers. These nanoscale reinforcements can be made of various materials such as ceramics, carbon nanotubes, graphene, or other nanoscale materials.

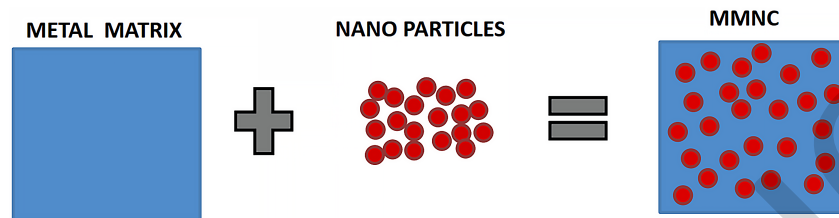


Figure 39

The addition of these nanoscale reinforcements (fillers) can significantly enhance the mechanical (hardness, tensile strength, creep behaviour,...), thermal, electrical, tribological (wear resistant, coefficient of friction,...) and other properties of the metal matrix.

6.1 Materials

The most studied **metal matrix** materials are Al, Mg, Ti, Cu alloys and steels, while for **nano particles** the materials (particle size is between 20 and 70 nm) are:

- **Oxides** → Al_2O_3 , Y_2O_3 ,...
- **Carbides** → SiC , TiC , B_4C ,...
- **Nitrates** → AlN , Si_3N_4 ,...
- **Borides and Hydrides** → TiB_2 , TiH_2 ,...
- **Intermetallic compounds** → Al_3Ti , NiTi , AlCa
- **Carbon** → Carbon Black (CB), Diamonds, Carbon Nanotubes (CNTs), Carbon Nanohorns (CNHs), C_{60} and C_{70} fullerene

6.1.1 Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) are cylindrical nanostructures made entirely of carbon atoms arranged in a hexagonal lattice. They can be thought of as rolled-up sheets of graphene, which is a single layer of carbon atoms arranged in a honeycomb pattern. There are several types of carbon nanotubes based on their structure (see Figure 40):

- **Single-Walled Carbon Nanotubes (SWNT)** ▶ Consist of a single layer of carbon atoms rolled into a seamless cylindrical structure. It exhibit exceptional mechanical properties such as high tensile strength (about 100 GPa) and stiffness (about 1 TPa) due to the strong covalent sp^2 bonds between carbon atoms within the hexagonal lattice.
- **Double-Walled Carbon Nanotubes (DWNT)** ▶ Consist of two concentric tubes of graphene, with one tube nested within the other. It exhibit excellent mechanical strength (about 63 GPa) and stiffness comparable to SWNT due to the additional layers, but they may also have slightly higher density (about 1.4 g/cm^3).

- **Multi-Walled Carbon Nanotubes (MWNT)** ▶ Consist of multiple concentric layers of graphene, akin to a series of nested tubes. It possess excellent mechanical properties, although they may not be as strong or stiff as SWCNTs due to defects and interlayer interactions.

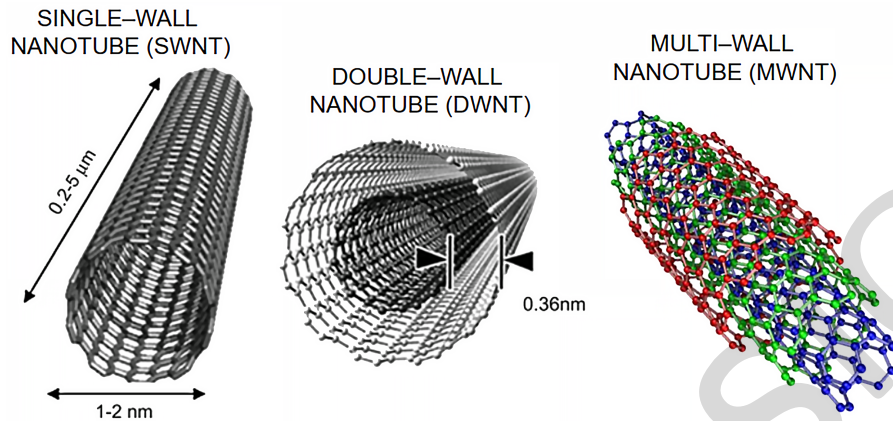


Figure 40: CNTs types

6.1.2 Carbon Nano-Horns (CNHs)

Carbon Nano-Horns (CNHs) are horn-shaped nanostructures composed of graphene sheets arranged in a conical or horn-like configuration.

They were first discovered in 1999 by a team of Japanese scientists (S. Iijima).

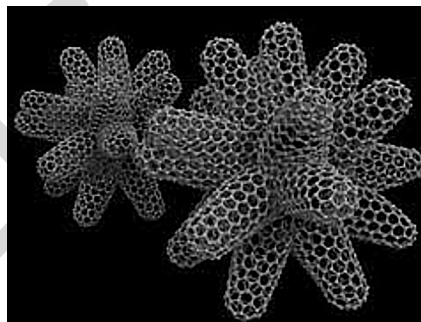


Figure 41: CNHs

CNHs are typically composed of graphene sheets rolled into a conical shape, resembling tiny horns (diameter 2 – 3 nm, average length 30 – 50 nm and aggregates ~ 80 nm).

- CNHs exhibit high surface area due to their complex structure, which makes them suitable for various applications, including gas storage, catalysis, and drug delivery.
- They possess excellent electrical and thermal conductivity, making them promising candidates for electronic and thermal management applications.

6.2 Strengthening mechanisms

The characteristics of metal matrix composite materials are determined by their microstructure and internal interfaces, which are affected by their production and thermo-mechanical history.

- **Matrix:**

- Chemical Composition ▶ The chemical composition of the matrix metal determines its inherent properties, such as strength, ductility, corrosion resistance, and thermal conductivity
- Grain Size ▶ Smaller grain sizes typically result in higher strength due to increased grain boundary strengthening mechanisms. Grain size can be controlled through various processing techniques such as mechanical milling, severe plastic deformation, or annealing treatments.
- Texture ▶ Texture refers to the preferred orientation of crystallographic planes within the matrix material. It can influence mechanical properties, anisotropy, and deformation behavior.
- Precipitates ▶ Precipitates are secondary phases that form within the matrix material during processing or heat treatment. Precipitates can act as obstacles to dislocation movement, leading to increased strength and hardness.
- Lattice Defects ▶ Lattice defects such as vacancies, interstitials, and dislocations play a crucial role in the mechanical behavior of the matrix material. Dislocations, in particular, are important in plastic deformation processes and can interact with nanoscale reinforcements.

- **Second Phase:**

- Volume Fraction ▶ The volume fraction of the second phase refers to the proportion of the composite occupied by the nanoscale reinforcement material. It is typically expressed as a percentage and can significantly influence the mechanical properties. Higher volume fractions of the second phase generally lead to greater reinforcement and improved mechanical performance, up to a certain point where excessive reinforcement may lead to processing difficulties or decreased ductility.
- Type of Particles ▶ The choice of reinforcement material depends on factors such as strength, stiffness, thermal conductivity, electrical conductivity, and compatibility with the matrix material.
- Size ▶ Nanoscale reinforcement particles typically have diameters ranging from a few nanometers to a few hundred nanometers. Smaller particle sizes generally lead to greater strengthening effects due to increased surface area and interface interactions with the matrix material.
- Distribution ▶ Ideally, the particles should be uniformly dispersed throughout the matrix to ensure consistent reinforcement and avoid clustering or agglomeration.
- Orientation ▶ Controlled alignment or orientation of particles may be desirable in certain applications to optimize mechanical performance along specific directions. Techniques such as directional solidification, magnetic alignment, or shear flow during processing can be used.

- **Internal Interfaces:** The adhesion between the metallic matrix and the nanoscale reinforcements is crucial for ensuring efficient load transfer and enhancing the mechanical properties of the composite. The interface between the matrix and reinforcements plays a significant role in controlling the dispersion, stability, and effectiveness of the reinforcements.

The main **strengthening mechanisms** for MMNCs include:

- Load-bearing effect

- Hall-Petch strengthening
- Work hardening
- CTE mismatch contribution
- EM mismatch contribution
- Orowan strengthening (just for MMNCs)

6.2.1 Load-bearing Effect

Load-bearing Effect

The **load-bearing effect** refers to the capability of the nanoscale reinforcements to carry a significant portion of the applied load, thereby enhancing the mechanical properties of the composite.

This effect is a fundamental mechanism that contributes to the improvement of strength, stiffness, and toughness.

The load-bearing effect relies on **efficient load transfer from the matrix to the reinforcements**. As the external load is applied, stress is transferred from the matrix to the reinforcements through interfacial bonding.

The load-bearing contribution of reinforcement can be expressed in the following way:

$$\Delta\sigma_l = v_p \cdot \sigma_m \left[\frac{(l + t) A}{4l} \right]$$

where v_p is the volume fraction, σ_m is the yield strength of the matrix, l is the size of particles parallel to load direction, t is the thickness of particles and $A = l/t$ is the aspect ratio. All these parameters refer to purely geometric aspects.

In particular, for equiaxial particle ($l = t$):

$$\Delta\sigma_l = 0.5v_p\sigma_m$$

and do not depend on particle size.

When it comes to nanocomposites, however, the percentage of particles is very low (around 2%), and therefore their contribution can be neglected:

$$\Delta\sigma_l = 0.01\sigma_m$$

6.2.2 Hall-Petch Strengthening

Hall-Petch Strengthening

The **Hall-Petch strengthening** describes the relationship between the grain size and the yield strength of a material.

Named after two scientists who independently proposed the concept, Cyril Hall and Norman Petch, this mechanism is crucial in understanding the mechanical behavior of materials, particularly in nanocrystalline and ultrafine-grained materials.

Grain boundaries are interfaces between adjacent grains where atoms are less densely packed and exhibit higher energy compared to the atoms within the grain. These boundaries act as barriers to dislocation motion and influence the material's mechanical properties.