Mo

Molybdenum

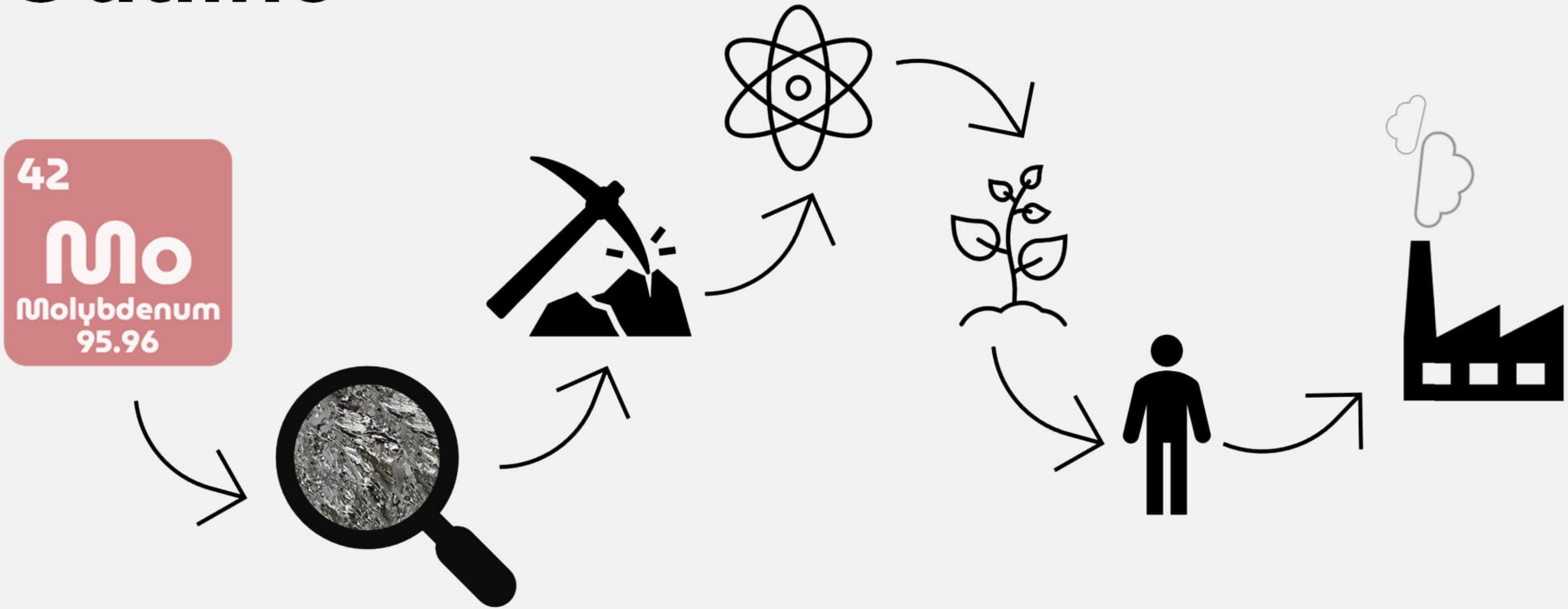
Maryam Jafari

Saara Siekkinen

25.9.2023

Aalto-yliopisto
Aalto-universitetet
Aalto University

Outline

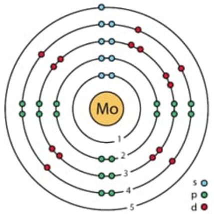


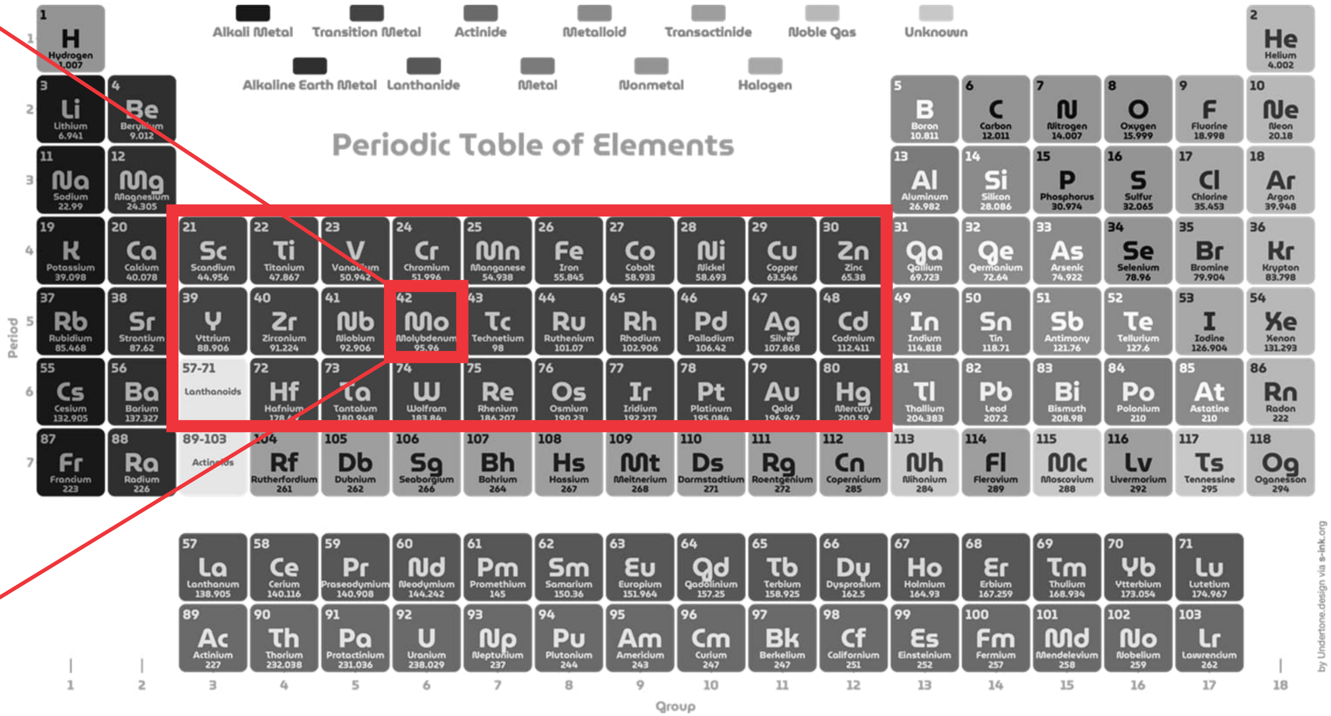
Aalto-yliopisto
Aalto-universitetet
Aalto University

Molybdenum in the Periodic Table

Electronic configuration:

$1s^2$
$2s^2\ 2p^6$
$3s^2\ 3p^6\ 3d^{10}$
$4s^2\ 4p^6\ 4d^5$
$5s^1$

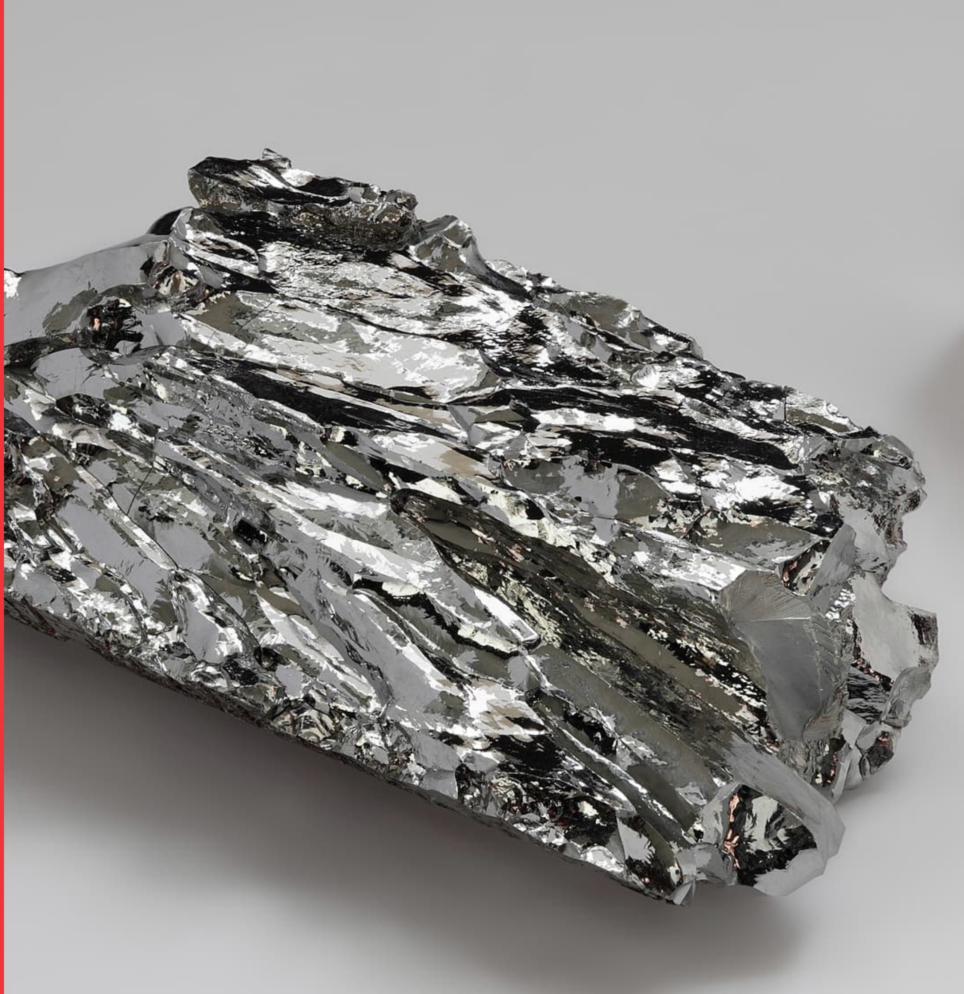




Aalto-yliopisto
Aalto-universitetet
Aalto University

Discovery

- The name is based on Ancient Greek, “Molybdos”, meaning lead-like
- First Discovered by Carl Welhelm Scheele, a Swedish chemist, in 1778
- Molybdenum was isolated by Peter Jacob Hjelm in 1781

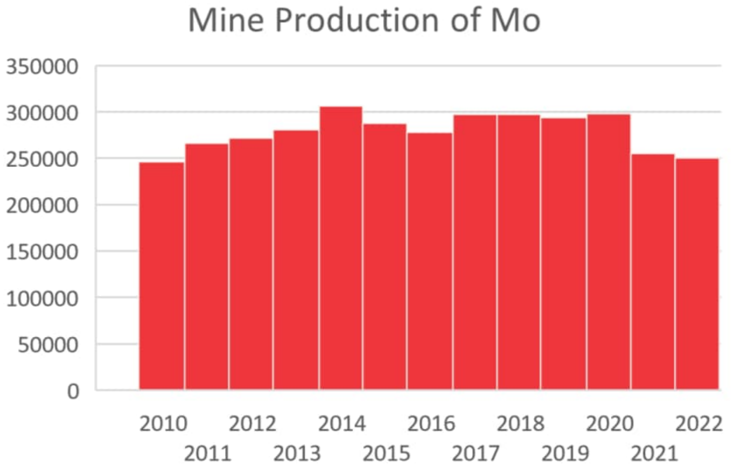


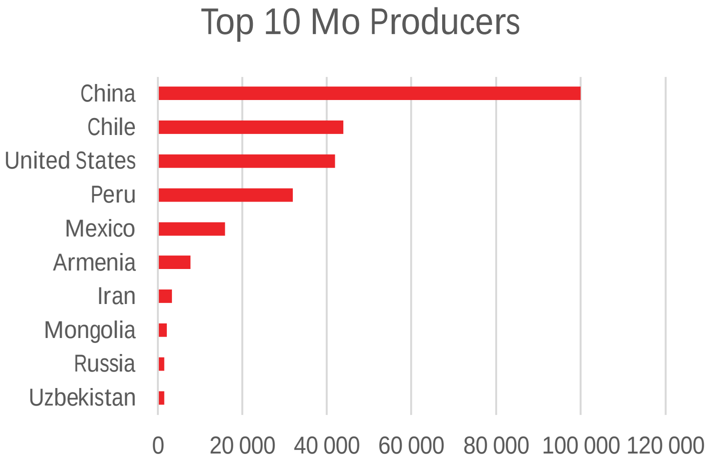
Aalto-yliopisto
Aalto-universitetet
Aalto University

Lide, David R., ed. (1994). "Molybdenum". CRC Handbook of Chemistry and Physics.
Lepora N (2007) The Elements: Molybdenum. New York, USA; Marshall Cavendish. ISBN: 0761422013

Production

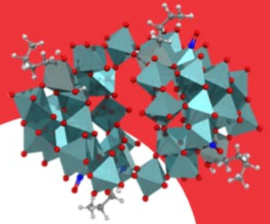
- Other elements are combined with Molybdenum in nature
- Most common form is MoS_2
- Usually found with sulfide minerals, notably Cu
- Mo mines are classified based on minerals in ore body:
    - Primary mines
    - By-product
    - Co-product mines





SS0

Properties of Molybdenum



42
Mo
Molybdenum
95.96

- Not found as a free metal, usually in minerals
- An essential trace element (co-factor)
- Metal alloys:
  - Strenght
  - Acid resistance

Chemical properties

- Electronegativity 2.16
- Oxidation states: -4, -2, -1, 0, +1, +2, +3, **+4**, +5, **+6**
- Low solubility in water, except MoO_4^{2-}

Physical properties

- Melting point 2623 °C (6th highest)
- Boiling point 4639 °C
- Density 10,28 g/cm^3
- High thermal and electrical conductivity

Isotopes

- 35 known isotopes
- Mo-98 most abundant isotope
- Mo-99, fission product

Geometry

- Octahedral or tetrahedral
- Complexes with anionic species

→ Colorful solutions (ascorbic acid)

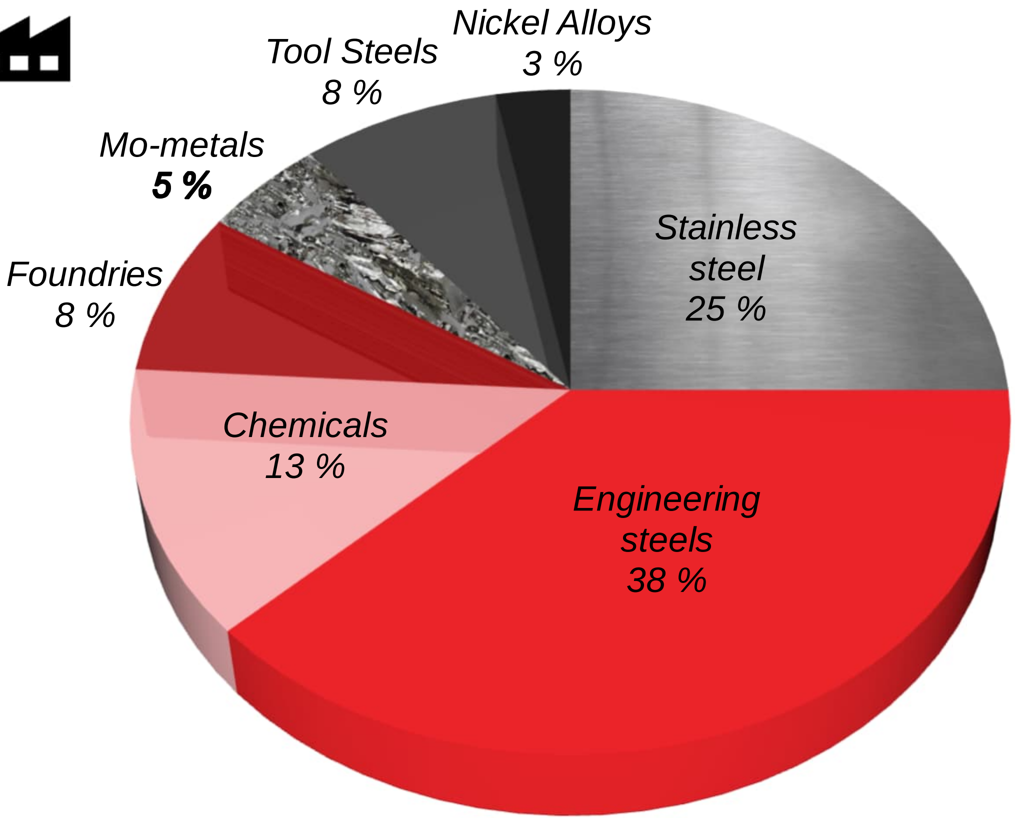
Aalto-yliopisto
Aalto-universitetet
Aalto University

SS0 https://woelen.homescience.net/science/chem/exps/colorfulmolybdenum/index.html

Siekkinen Saara; 2023-09-23T18:27:04.347

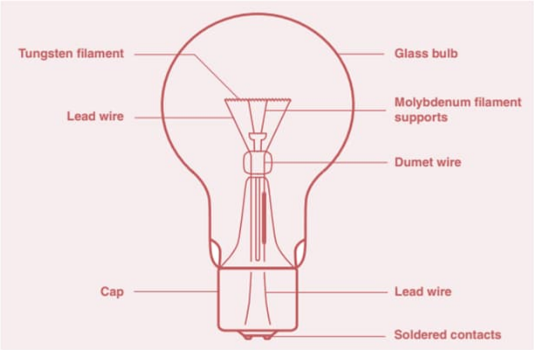
Application

- Steel and Alloys
- Chemical Industry
- Electrical and Electronic
- Medicine
- Agriculture



Aalto-yliopisto
Aalto-universitetet
Aalto University

The First Mo Application



- **Incandecent lighting (1940)**
- **Ideal to glass-to-metal seals**
- **Can be used in high intensity lamps and as a reflector**
  - High-temperature strength, mechanical stability, resistance to corrosion and low thermal expansion
  - Maintain the strength and stability up to 1900 °C
- **Today we mainly use compact fluorescent lamps (CFL) and light-emitting diode (LED) lamps**
  - Nowadays: support wire and glass feed-throughs in halogen lamps and as mandrel wire

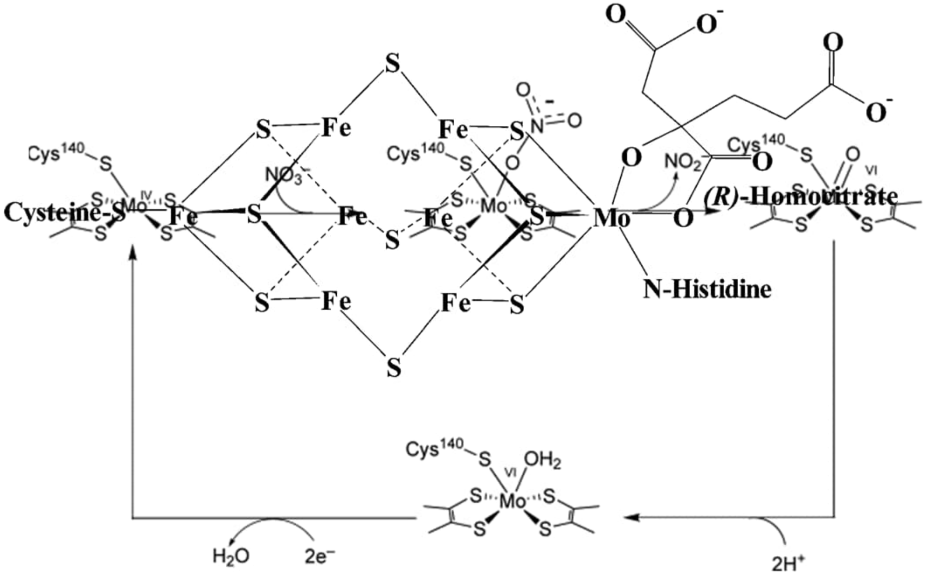
Molybdenum in Plants

- Molybdenum act as an electron carrier in enzymes
- Essential in plant enzymes
  - **Nitrogenase**: Enzymes in bacteria that reduce N_2 to NH_3 → nitrogen fixation

$$N_2 + 8e^- + 8H^+ \rightarrow 2NH_3$$

  - **Nitrate Reductase**: molybdoenzymes that reduce nitrate (NO_3^-) to nitrite (NO_2^-)

$$NO_3^- + 2H_2O + 2e^- \rightarrow NO_2^- + H_2O + OH^-$$



Aalto-yliopisto
Aalto-universitetet
Aalto University

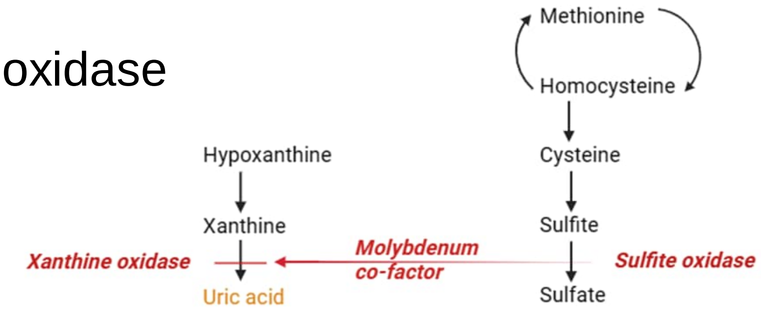
Reedijk, Jan, and Kenneth R. Poeppelmeier. "Comprehensive inorganic chemistry II: from elements to applications." (2013).

SS0

Molybdenum in Humans

SS1

- Molybdenum act as an electron carrier in enzymes
- Essential in human enzymes:
  - Needed for metabolism of sulfur amino acids
  - **Sulfite Oxidase**: **Mo** as co-factor, detoxification, catalyzes oxidation of sulfite (SO_3^{2-}) to sulfate (SO_4^{2-})
  - **Aldehyde oxidase**: **Mo** as co-factor, catalyzes the hydroxylation of some heterocycles, drug metabolism
  - **Xanthine oxidase**: **Mo** as co-factor, generates reactive oxygen species, uric acid formation
- MoCo dependent on xanthine and aldehyde oxidase
- Deficiency causes neurological symptoms



Slide 10

SS0 https://www.sciencedirect.com/topics/pharmacology-toxicology-and-pharmaceutical-science/aldehyde-oxidase
Siekkinen Saara; 2023-09-23T14:42:55.818

SS1 https://www.youtube.com/watch?v=-7Hez86w7-I
Siekkinen Saara; 2023-09-23T14:47:22.236

Steel and Alloys

- Steel is classified by its composition:
  - **Carbon Steel**
  - **Stainless Steel**
  - **Alloy Steel**
  - **Tool Steel**

Steel and Alloys

- Steel is classified by its composition:

Carbon Steel	Iron-base alloy with only 2% or less carbon
Stainless Steel	
Alloy Steel	
Tool Steel	

Steel and Alloys

- Steel is classified by its composition:

Carbon Steel	Iron-base alloy with only 2% or less carbon
Stainless Steel	Iron-base alloy that contain at least 10.5% chromium Resist staining or Rusting
Alloy Steel	
Tool Steel	

Steel and Alloys

- Steel is classified by its composition:

Carbon Steel	Iron-base alloy with only 2% or less carbon
Stainless Steel	Iron-base alloy that contain at least 10.5% chromium Resist staining or Rusting
Alloy Steel	Ni, Cu, Cr or Al are added to alloy enhances the strength, ductility, corrosion resistance
Tool Steel	

Steel and Alloys

- Steel is classified by its composition:

Carbon Steel	Iron-base alloy with only 2% or less carbon
Stainless Steel	Iron-base alloy that contain at least 10.5% chromium Resist staining or Rusting
Alloy Steel	Ni, Cu, Cr or Al are added to alloy enhances the strength, ductility, corrosion resistance
Tool Steel	W, Mo, Co, and V are added to the alloy enhances heat resistance and overall durability Excel in cutting and drilling equipments

Mo in Alloys

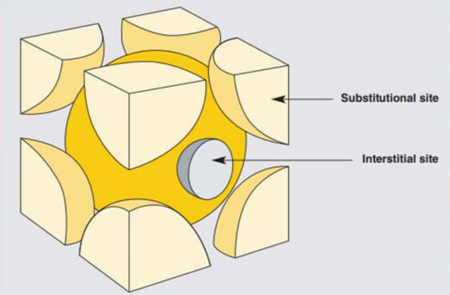
- Adding Molybdenum to different steel and alloys:

Carbon Steel
Stainless Steel
Alloy Steel
Tool Steel

- Divided into 2 classes:
  - **corrosion-resistant alloys**: resistance to nonoxidizing environments such as the halide acids and sulfuric acid
  - **high temperature alloy**: impart resistance to damage caused by high temperature creep.
    - **Solid-solution strengthened**: As molybdenum diffuses very slowly in nickel and high temperature creep is generally diffusion controlled, adding of molybdenum can reduce creep rates.
    - **Age-hardanable**: This alloys utilize the precipitation of gamma-prime and molybdenum additions strengthen the matrix and reduce the lattice mismatch between the matrix and the gamma-prime particles.

Mo in Steel

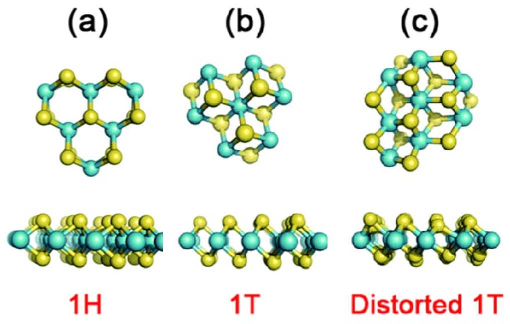
- Carbon Steel
- Stainless Steel
- Alloy Steel
- Tool Steel



Mo	Min. 99.95–99.97 Mo (depending on the producer)	Constitutes the majority of Mo metal products: furnace and glass melting components, power semiconductor heat sinks, sputtering targets used to manufacture thin films in flat-panel displays and thin-film solar cells, powders spray-dried with either organic binders for high-speed pressing, or ADM for thermal spray applications
Alloys		
Substitutional alloys		
Mo-W	10–50 W	Equipment for handling molten Zn, glass stirrers
Mo-Re	3 Re, 5 Re, 41–47.5 Re	Thermocouples (low Re) and applications requiring low-temperature ductility (high Re)
Mo-Ta	10.7 Ta	Thin films in touch-screen displays
Mo-Nb	3.0–9.7 Nb	Thin films in touch-screen displays
Carbide-stabilized alloys		
TZM	0.5 Ti-0.08 Zr-0.03 C	Isothermal forging dies, injection molding tooling, metalworking tools, X-ray targets
MHC	1.2 Hf-0.08 C	Extrusion dies, metalworking tools
Dispersion-strengthened alloys		
Mo-La_2O_3	0.43–1.20 La, 0.075–0.21 O	Furnace heating elements, sintering boats, lamp components
Mo-ZrO_2	1.24 Zr, 0.43 O	Glass-melting furnace components
Mo-Y_2O_3-Ce_2O_3	0.37–0.43 Y, 0–0.06 Ce, 0.11–0.12 O	Halogen lamp components, evaporation boats
K/Si doped	0.01–0.07 Si, 0.005–0.03 K, 0.01–0.07 O	Lamp components, heating elements
Composite materials		
Laminates		
Cu-Mo-Cu	Various Cu/Mo ratios possible; typically between 13% and 25% Cu thickness per side	Heat sinks for semiconductors and integrated circuits
Mo-Ni	Typically 5% Ni thickness bonded to one side	Power semiconductor heat sinks
Powder composites		
MoCu	15 Cu, 30 Cu	Heat sinks for power integrated circuits: hybrid vehicles, mobile telephone cell transmitters
Mo-Ti	50 atomic % Ti	Sputtering targets to manufacture thin films in flat-panel displays and thin-film photovoltaic devices
Mo-Na	1–3 Na	Sputtering targets to manufacture electrodes in thin-film photovoltaic devices
Thermal spray powders		
Pure Mo	99.0 Mo	Piston rings, synchro rings, continuous casting & ingot molds
Mo-C	Up to 6 C	Piston rings, synchro rings, pump impeller shafts
17.8Ni-4.3Cr-1.0Si-1.0Fe-0.8B	17.8 Ni-4.3 Cr-1.0 Si-1.0 Fe-0.8 B	Piston rings, synchro rings

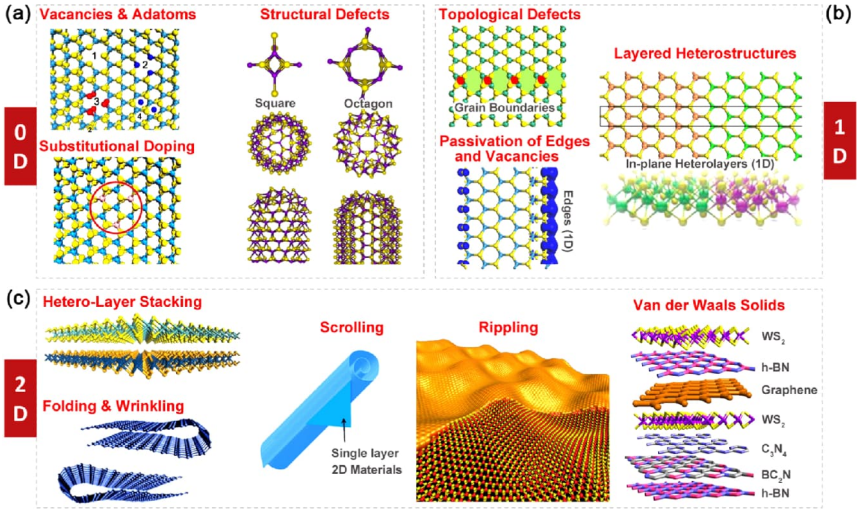
Defects in Transition Metal Dichalcogenide

- Two possible structures for monolayer of MX_2 (M= Mo, W, X=S,Se)
  - the semiconducting trigonal prismatic phase: 1H phase
  - the metallic octahedral prismatic phase: 1T phase
    - In some cases, the 1T phase is not thermodynamically stable, and the structure 1T' can be observed instead



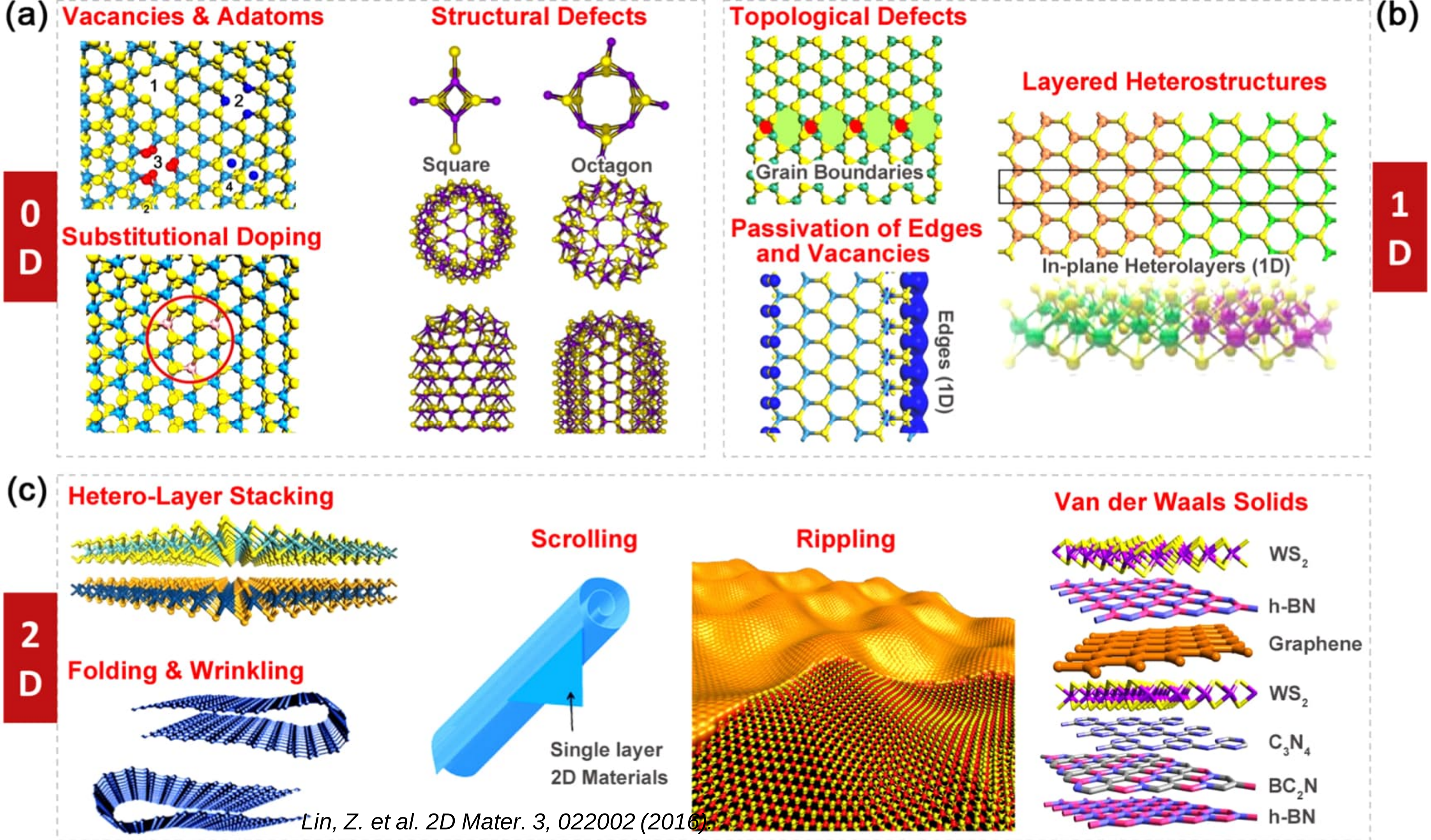
Chalcogen atoms are shown in yellow, and transition metal atoms are shown in blue

- Defects in 2D crystals can be classified based on their dimensionality:
  - Zero-dimensional (point defects)
  - One-dimensional (grain boundaries)
  - Two-dimensional



Aalto-yliopisto
Aalto-universitetet
Aalto University

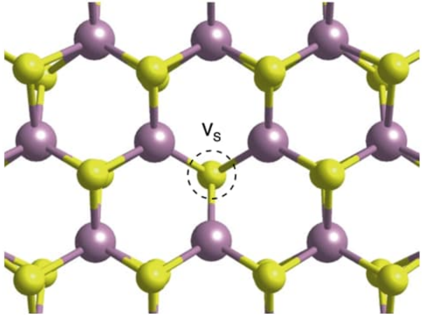
Lin, Z. et al. 2D Mater. 3, 022002 (2016).



Lin, Z. et al. 2D Mater. 3, 022002 (2016).

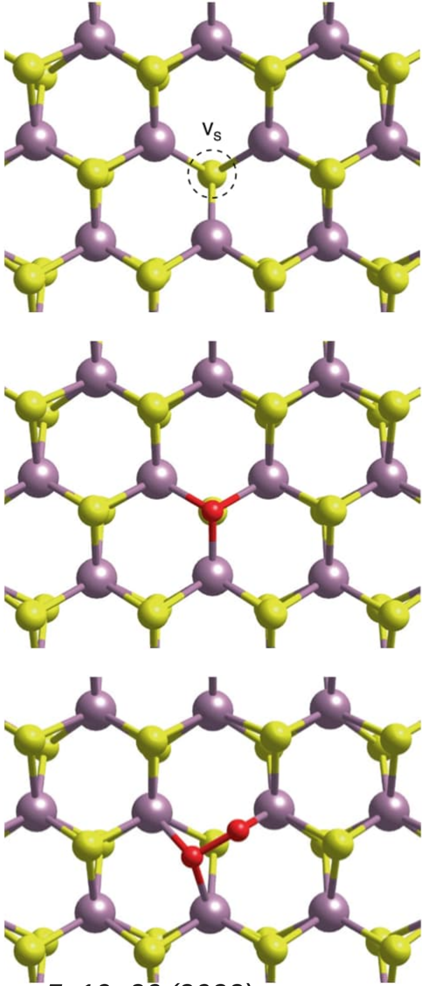
MoS_2 Defects

- Chalcogen defect in metal dichalcogenide result in low performance in electronic devices
- Defects can affect the physical properties.
- Creating tailored applications by using defects
- Defect engineering via chemical doping:
  - After the growth of 2D material
  - During the growth of 2D material
    - Doping during the growth of the material result in dopant atom be covalently bonded to the crystalline lattice – making it more resilient to harsher environments
    - Covalently bonded oxygen can be used to passivate native chalcogen monovacancies



Das, S., Elías, A.L. Leaving defects out of 2D molybdenum disulfide. Nat Electron ***5****, 19–20 (2022).*

Engineering MoS_2 Defects



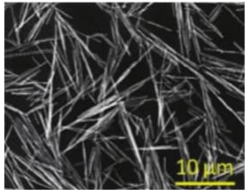
- High density of chalcogen vacancies prevents the formation of ohmic contacts at the metal/semiconductor interfaces and lead to
  - High contact resistance
  - Scattering sources
  - Reduced carrier mobility
  - Unintentional doping
- An oxygen-incorporated chemical vapor deposition technique was used
  - passivates sulfur vacancies
  - Suppress the formation of donor states in MoS_2
- This was achieved due to the formation of Mo-O bonding at the vacancy sites.
- Contact Resistance was lowered to 1 kΩ µm.

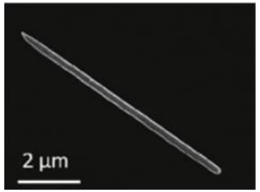
Aalto-yliopisto
Aalto-universitetet
Aalto University

Das, S., Elías, A.L. Leaving defects out of 2D molybdenum disulfide. Nat Electron ***5****, 19–20 (2022).*

Assembly and Fabrication of MoS_2 Nanostructures

- Superior electronic properties
- Highly promising material for (opto)electonics, catalysis, energy storage, water treatment and gas sensing or biochemical sensoring
- High research in transition metal dichalcogenides (TMD)
  - Single crystal MoS_2 nanoflakes possess edge sites and in plane sulfur vacancies **outstanding catalytic activity**
  - Semi-conductor → electric conductivity can be tuned





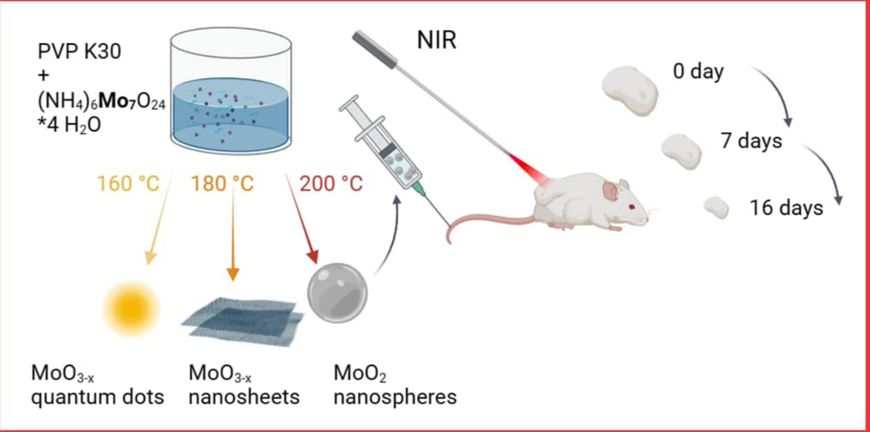
- Thin films have been synthesized via CVD and hydrothermal growth
- Tubular or core-shell nanotructures can be grown via catalyzed transport reaction
  - Demand of controlled fabrication of nanostructures
- Synthesized MoS_2 show high thermal stability and no morphological changes can be observed even after several high temperature treatments
- Nanoribbons can be fixed on the substrate upon UV light exposure
  - High accuracy in position and angle
  - Assembly of MoS_2 device
  - Can be used in new applications

Huang Yun "Scalable Fabrication of Molybdenum Disulfide Nanostructures and their assembly." (2020)

Mo Future Application in Cancer Therapy

- **Transition metal oxides: MoO_2 and MoO_3**
  - Unique, localized surface plasmon resonance effects (SPR) → **adducts for photothermal cancer therapy**
  - Function via modulation/exchange of multiple intervalence charge-transfer via chemical alterations
  - Great absorption and photoconversion properties in NIR region → **photothermal/photoablation therapy**

- **Transition metal dichalcogenides: consist of MoS_2**
  - Can be characterized as 2-D or 3-D nanomaterial → **medical application, imaging probes**
  - Excellent electrical properties, conductivity and biocompatibility, superior charge-density-wave transition
  - Inserting Mo sheets between sulfur sheets → nanotructures have ability to get in cells via endosomal uptake → **drug delivery system**



Dhas Namdev "Molybdenum-based hetero-nanocomposites for cancer therapy, diagnosis and biosensing application: Current advancement and future breakthroughs." (2021).

THANK YOU!

aalto.fi

Aalto-yliopisto
Aalto-universitetet
Aalto University

Mo in Carbon Steel

- Adding Molybdenum to different steel and alloys:

Carbon Steel

Stainless Steel

Alloy Steel

Tool Steel

- Improve hardenability of carbon steels
- Mo_2C nano-sized particles contributes to secondary hardening
- The secondary hardening effect of molybdenum during tempering adds to the solute effect retaining part of the dislocation density.
  - an important function of molybdenum in high-speed steels
- It also allows achieving the desired strength level at reduced carbon equivalent and improving weldability.
- Anti-embrittlement effects of Molybdenum:
  - Temper embrittlement may occur when steels are slowly cooled after tempering through the temperature range between 450 and 550°C

Mo in Stainless Steel

- Adding Molybdenum to different steel and alloys:

Carbon Steel

Stainless Steel

Alloy Steel

Tool Steel

- Increases corrosion resistance
  - Used in chemical processing plant or marine applications
- increases the elevated temperature strength of stainless steels through solid solution hardening
  - Used in heat exchangers and other elevated temperature equipment such as in automotive exhaust systems

Mo in Alloy Steel

- Adding Molybdenum to different steel and alloys:

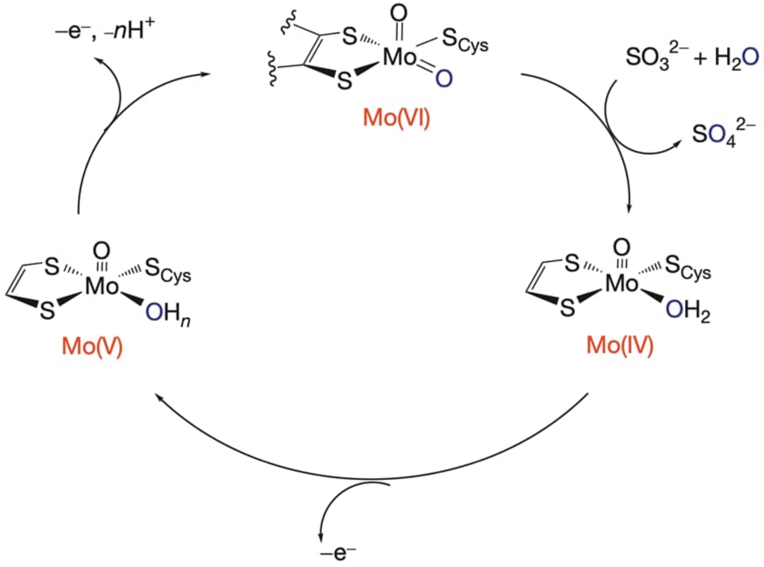
Carbon Steel

Stainless Steel

Alloy Steel

Tool Steel

- Divided into 2 classes:
  - corrosion-resistant alloys: resistance to nonoxidizing environments such as the halide acids and sulfuric acid
  - high temperature alloy: impart resistance to damage caused by high temperature creep.
    - solid-solution strengthened: As molybdenum diffuses very slowly in nickel and high temperature creep is generally diffusion controlled, additions of molybdenum are quite effective in reducing creep rates.
    - age-hardanable: This alloys utilize the precipitation of gamma-prime and molybdenum additions strengthen the matrix and reduce the lattice mismatch between the matrix and the gamma-prime particles.



−e⁻, −nH⁺
S
O
Mo
S_{Cys}
S
O
Mo(VI)
SO_3^{2-} + H_2O
SO_4^{2-}
S
O
Mo
S_{Cys}
S
OH_n
Mo(V)
S
O
Mo
S_{Cys}
S
OH_2
Mo(IV)
−e⁻