FS 2024/25

MSE-422 – Advanced Metallurgy

10-The precious metals

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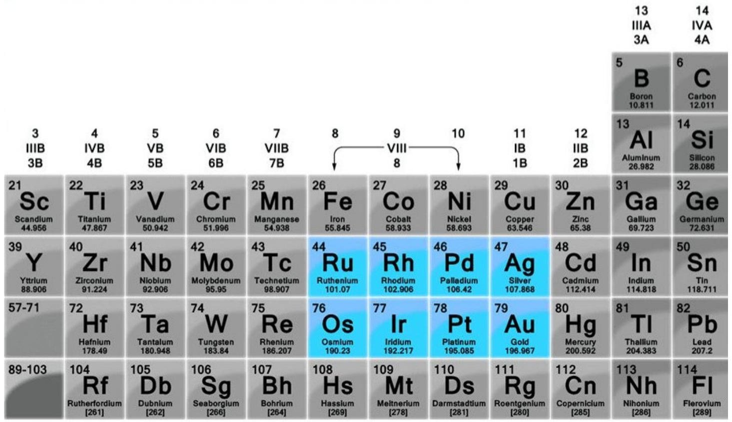
What are precious metals?

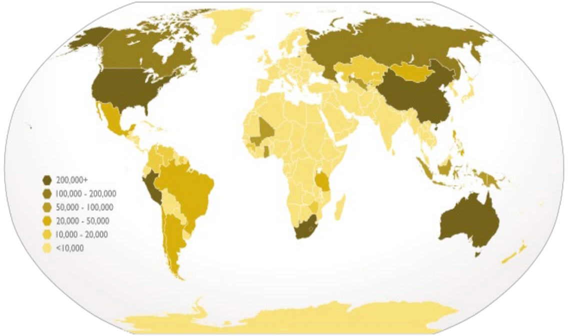
EPFL

- Precious metals include gold, silver, and the platinum group metals (PGM): Ru, Rh, Pd, Os, Ir, and Pt.
- PGMs are further divided into "light" (Ru, Rh, Pd) and "heavy" (Os, Ir, Pt) groups.
- These metals are considered noble metals due to their position in the electrochemical series relative to the hydrogen electrode.
- They are precious because they are rare, expensive, and inert, allowing them to hold high value in small volumes



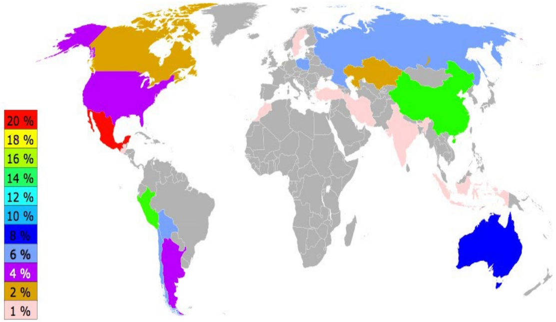
Gold fact sheet

- Occurrence: 1-10 ppb in earth crust, primary resources in hydrothermal veins as native metal, secondary in sediments, and traces in Cu ores
- Reserves: Gold is everywhere in low concentration. Economic deposits are at > 0.5 ppm concentration (≈60 tons of deposit for 1 oz of fine gold)
- Main producers: China, Australia, Peru, US, South Africa, Russia, Canada
- Annual production: 3000 t; currently stored gold reserves: 30’000 t (banks), 150’000 t (industry and private).
- Price: 75 kUS$/kg (Nov. 2024)
- Main uses: Jewelry (50%), Coins (20%), Electronics (10%), Dental
- Physical properties: Melting point: 1337 K
  Boiling point: 3130 K
  Electrical resistivity: 2.17 μΩcm
  Thermal conductivity: 317 W/mK
  Atomic radius: 0.1442 nm
  Crystal structure: fcc



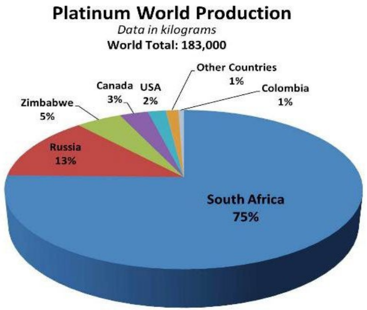
Silver fact sheet

- Occurrence: 70-80 ppb in earth crust, native as gold-silver alloy, by-product of Zn and Pb mining, traces in Cu ore.
- Reserves: Worldwide reserves estimated at 530’000 t
- Main producers: Mexico, China, Peru, Russia, Australia, Bolivia, Chile
- Annual production: 28’000 t (mining) + 6’000 t (recycling)
- Price: 950 US$/kg (2024)
- Main uses: Jewelry (20%), Coins (25%), Electronics (22%), Silverware (6%), Brazing (5%), Photovoltaics (5%)
- Physical properties: Melting point: 1234 K
  Boiling point: 2436 K
  Electrical resistivity: 1.58 µΩcm
  Thermal conductivity: 429 W/mK
  Atomic radius: 0.1443 nm
  Crystal structure: fcc



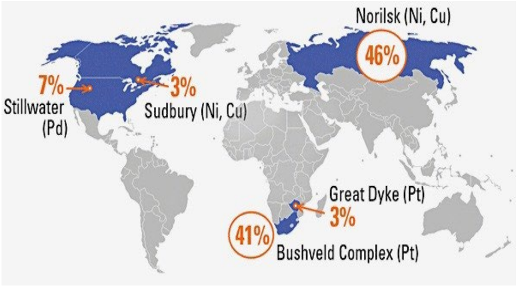
Platinum fact sheet

- **Occurrence** — 4 ppb in earth crust, sometimes as native metal, otherwise in Cu and Ni ores or as sulfides, arsenides, antimonides, and tellurides
- **Reserves** — 7’000 t (>90% in South Africa)
- **Main producers** — South Africa, Russia, Zimbabwe, Canada, US
- **Annual production** — 183 t (mining) + 60 t (recycling)
- **Price** — 25-30 kUS$/kg (Nov. 2024)
- **Main uses** — Catalysis (45% CO—CO_2), Jewelry (35%), Glassmaking and Chemical industry (10%)
- **Physical properties** — Melting point: 2041 K
  Boiling point: 4098 K
  Electrical resistivity: 10.7 µΩcm
  Thermal conductivity: 72 W/mK
  Atomic radius: 0.1386 nm
  Crystal structure: fcc



Palladium fact sheet

- Occurrence: 6 -15 ppb in earth crust, alloyed with platinum and also present in same ores; byproduct of Cu and Ni mining (anode dust in copper refining)
- Reserves 7’000 t
- Main producers South Africa, Russia, US, Canada
- Annual production 200 t (mining) + 70 t (recycling)
- Price 30 kUS$/kg (2024) – up to 85 kUS$/kg in 2022
- Main uses Catalysis (78% CO—CO2), Electronics (10%), Chemical industry (4%), Dental (5%), Jewelry (2%)
- Physical properties Melting point: 1825 K
  Boiling point: 3237 K
  Electrical resistivity: 10.5 µΩcm
  Thermal conductivity: 72 W/mK
  Atomic radius: 0.1347 nm
  Crystal structure: fcc



Iridium fact sheet

- Occurrence: 0.1 – 1 ppb in earth crust, native as IrOs or OsIr alloy, mining as accompanying Pt resources, and Cu and Ni ores
- Reserves: n.a.
- Main producers: South Africa, Russia, US, Canada
- Annual production: 3t
- Price: 137 kUS$/kg (2024)
- Main uses: Chemical industry (crucibles), spark plugs, fountain pen nibs
- Physical properties: Melting point: 2716 K
  Boiling point: 4701 K
  Electrical resistivity: 5.5 µΩcm
  Thermal conductivity: 147 W/mK
  Atomic radius: 0.1356 nm
  Crystal structure: fcc

Ruthenium fact sheet

- Occurrence: 1 ppb in earth crust, by-product of Pt mining and traces in Cu and Ni ores
- Reserves: 5000 t
- Main producers: South Africa, Russia, US, Canada
- Annual production: 12 t
- Price: 14’000 US$/kg (2024)
- Main uses: Chemical Industry, Thick film resistors (RuO_2), Data recording devices, Ni-Superalloys
- Physical properties: Melting point: 2523 K
  Boiling point: 4423 K
  Electrical resistivity: 7.3 μΩcm
  Thermal conductivity: 120 W/mK
  Atomic radius: 0.1340 nm
  Crystal structure: hcp

Rhodium fact sheet

- Occurrence: 0.5 – 1 ppb in earth crust, essentially accompanying Pt resources and Cu and Ni ores
- Reserves: n.a.
- Main producers: South Africa, Russia, US, Canada
- Annual production: 30 t
- Price: 150-170 kUS$/kg (2024)
- Main uses: Catalyst (80% NOx), Jewelry coatings (10%), Chemical industry (10%)
- Physical properties: Melting point: 2236 K
  Boiling point: 3970 K
  Electrical resistivity: 5.1 µΩcm
  Thermal conductivity: 150 W/mK
  Atomic radius: 0.1369 nm
  Crystal structure: fcc

Osmium fact sheet

- Occurrence: 1-2 ppb in earth crust, essentially accompanying Pt resources and Cu and Ni ores, native in OsIr and IrOs alloys
- Reserves: n.a.
- Main producers: South Africa, Russia, US, Canada
- Annual production: <<1 t
- Price: 15’000 kUS$/kg (but no market)
- Main uses: Osram (Os + W) (before LED era), Fountain pens, electrical contacts (wear), density standards
- Physical properties: Melting point: 3300 K
  Boiling point: 5285 K
  Electrical resistivity: 9 µΩcm
  Thermal conductivity: 88 W/mK
  Atomic radius: 0.1337 nm
  Crystal structure: hcp

Separation of precious metals

Gold (Au):

- Can dissolve as $AuCl_4^-$; becomes insoluble as pure Au.
- Requires specific chemical conditions to separate from other elements.

Silver (Ag):

- Dissolves in $AgNO_3$; further steps make it insoluble.
- Key reagents like NaCl and AgCl are used to produce stable, insoluble forms.

Platinum (Pt):

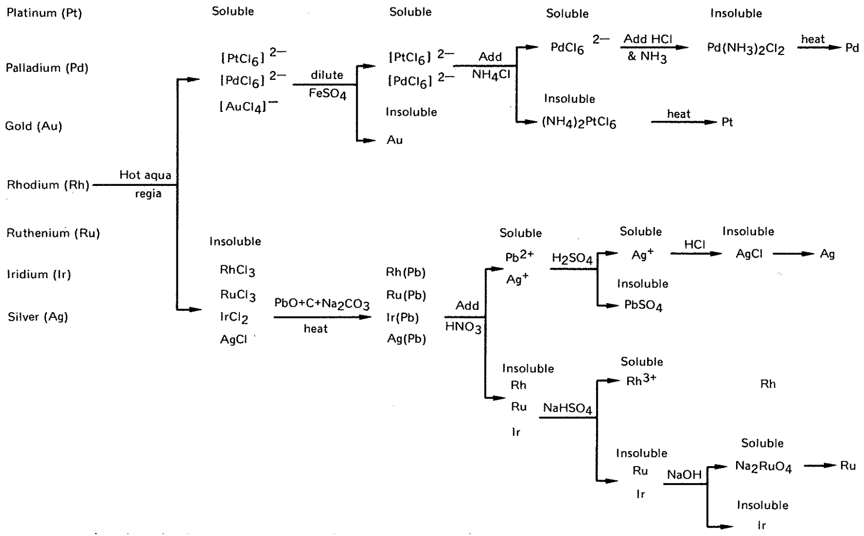
- Soluble in solutions forming $PtCl_6^{2-}$ or $(NH_4)_2PtCl_6$ complexes.
- The separation process ends with forms that are insoluble.

Palladium (Pd):

- Dissolves as $PdCl_4^{2-}$ or $[Pd(NH_3)_4]Cl_2$.
- Separation results in a final, insoluble form of Pd.

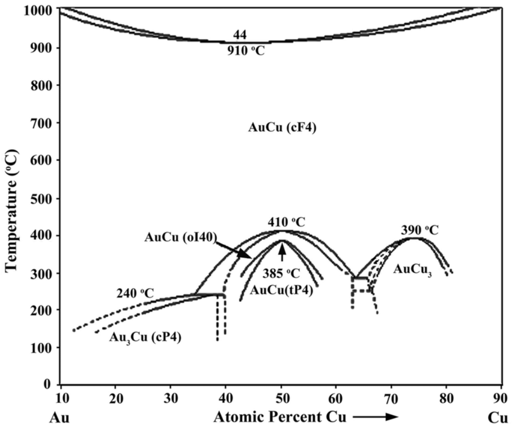
Iridium (Ir):

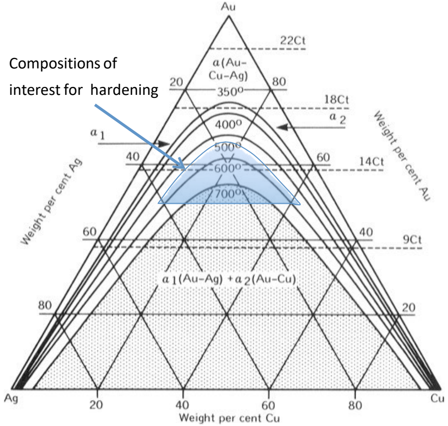
- Generally insoluble, but can dissolve as $IrCl_6^{2-}$ in certain conditions.
- Follows a separation path similar to other platinum group metal



The metallurgy of gold

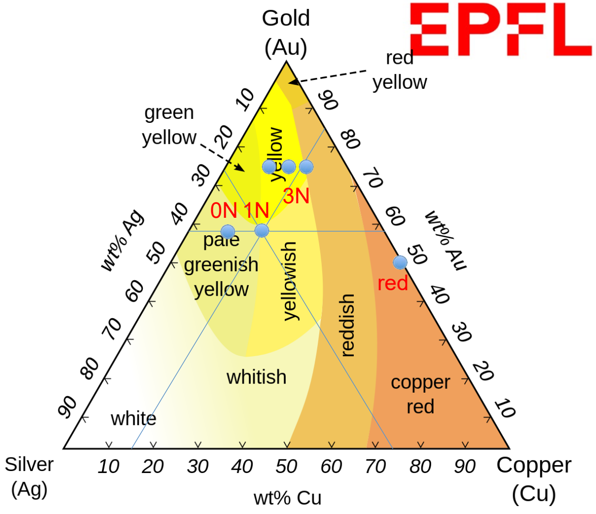
- Au alloys are regulated by Hallmarking standards defining their gold content given in parts per thousand, ‰, or in carats, both with regard to the weight.
- 1000 ‰ correspond to 24 carats. A 14 ct gold alloy has hence 585 wt.- ‰.
- Typical commercial standards are 24 ct, 20 ct, 18 ct, 15 ct, 14 ct, 12 ct, 10 ct, 9 ct and 8 ct. (N.B.: not to be confused with the weight units for gemstones, where 1 ct is 0.2 g)
- The main technical alloying elements for gold are Cu, Ag, Pd, Ni, and Zn.
- Alloying elements are added to gold to increase the mechanical strength and to adjust the color.





The metallurgy of gold

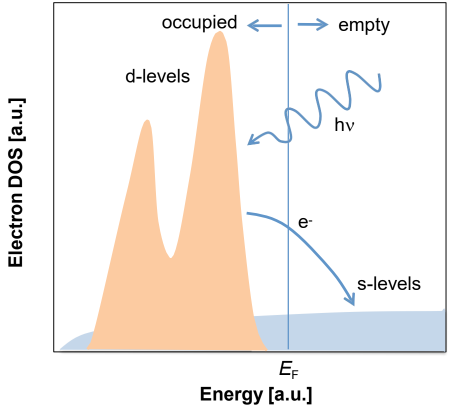
- The main application of gold alloys is in jewelry.
- the color of gold alloys is strongly affected by the composition
  - Ag increases the color changes from yellow to greenish-yellow to white.
  - Cu shifts the color from red-yellow to reddish to copper red
- In order to classify the colors, the N-scale has been developed as comparative scale.
  - 0N corresponds to a greenish yellow
  - with increasing N value a transition to reddish yellow is made.
  - The transitions are not sharp but rather continuous
- Some intermetallics of Au have completely different colors.

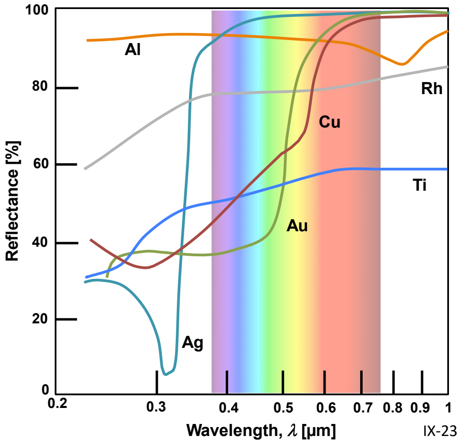


Alloy	Au	Ag	Cu	Al	Fe	In	Co
1N	58.5	26.5	15				
2N	75	16	9				
3N	75	12.5	12.5				
4N	75	9	16				
0N	58.5	34	7.5				
Red	50		50				
Blue	75				25		
Blue	46					54	
Purple	80			20			
Black	75						25

The colors of Au alloys

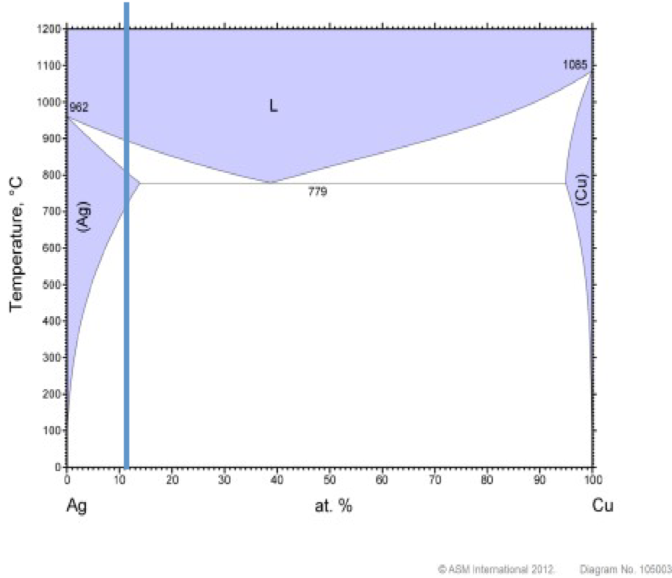
- For metals color comes from the selective absorption of certain wavelengths of the visible spectrum
- Absorption will happen when electrons can be excited from an occupied level to an empty level above the Fermi energy
- Ag, Al, Rh, and Ti exhibit little variation in reflectivity throughout the visible spectrum
- Cu and Au have a sharp drop in the orange and the yellow range → Au and Cu reflect yellow and, while they absorb significant amounts of green and blue
- For alloys, the reflectance (or, inversely, the absorption) will evolve between the two colors of the constituents.





The metallurgy of silver

- Pure silver is very soft and needs to be alloyed for “structural” use The most common alloying element for silver is copper
- Ag-Cu alloys are hardenable by solutionizing and precipitation of fine Cu in Ag (@300°C). Silver with 20 wt.-pct of Cu (Ag800) is even harder but is no longer white and needs to be plated.
- Recognized hallmarking standards (in weight fraction) for silver vary from country to country
  - 958.4/1000 (Britannia)/UK
  - 950/1000 (Minerva)/France
  - 925/1000 (Sterling)/UK
  - 920/1000 (Mercury 1)/France
  - 900/1000 (Coin)/US



The metallurgy of silver

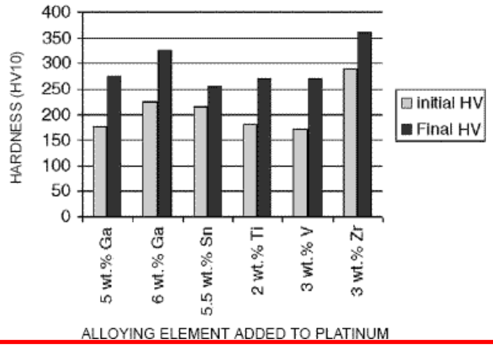
- Silver oxidizes readily, yet the oxide becomes unstable above 200°C. At higher temperature and in the liquid, silver dissolves significant amounts of oxygen that can lead to solidification defects (bubbles due to change in solubility for oxygen)
- The oxide formed with the alloyed copper remains stable and needs to be cleaned off
- Main problem with silver both for jewelry and silverware is tarnishing (formation of silver sulfide Ag_2S); it can be removed chemically (e.g. hot water + acetic acid + aluminium foil) or mechanically (silver polish)
- In order to prevent silver from tarnishing silver jewelry items are coated with rhodium → bright white color
- Alloying to protect from tarnishing would be preferred (permanent effect, does not wear off). Small amounts of Ge can be used to that effect, but are not widely used industrial practice

The metallurgy of Platinum

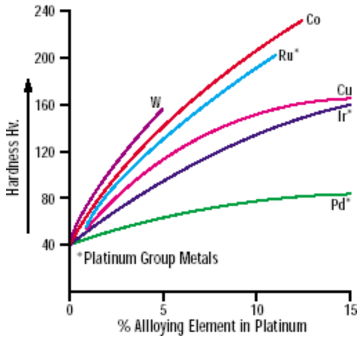
- Platinum Hallmarking standards are much more restrictive than their gold counterparts.
- Accepted standards are Pt950, Pt900, Pt850 and Pt800 (in CH mostly Pt950) → there is much less room to improve the intrinsic softness of platinum alloys by alloying
- Platinum alloys have typically very high melting points rendering the investment casting of platinum much less a large scale process than for gold.

5% Copper	Pt950/Cu	Melting Range 1725° C 1745° C	Hardness 120	Density g/cm3 20.0	General purpose Medium Hard Can be cast
3% Cobalt 7% Palladium	Pt900/Co/Pd	1730° C 1740° C	125 as cast	20.4	Hard Casting
5% Cobalt 10% Palladium	Pt850/Pd/Co	1710° C 1730° C	150 as cast	19.4	Harder Casting
5% Iridium 10% Iridium 15% Iridium	Pt950/Ir Pt900/Ir Pt850/Ir	1780-1790° C 1780-1790° C 1780-1790° C	80 110 160	21.4 21.5 21.5	General purpose Catches, Pins Springs, Watches
5% Palladium 10% Palladium 15% Palladium	Pt950/Pd Pt900/Pd Pt850/Pd	1755-1765° C 1740-1755° C 1730-1750° C	60, 68 as cast 80, 72 as cast 90, 64 as cast	20.6 19.8 19.1	Casting, delicate General purpose Chain making

Age hardenable alloys

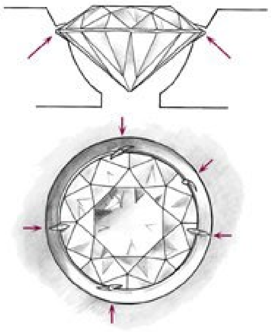


Solid solution strengthened alloys



Requirements for precious metals in jewelry

- Requirements for precious metals depend somewhat on application and the applied processing route
- In all cases, the alloy should maintain its visual appeal. i.e. unchanged color and shininess on long term
- For cast structures (e.g. ring investment casting):
  - Good fluidity and good form filling (in Gold: by Zn additions)
  - Low melting temperature (Pt problematic)
  - Grain refining (improved ductility)
  - Medium strength (stone insertion)
- For wrought applications (e.g. watch cases):
  - Ductility
  - Hardness (scratch resistance)



Flush setting requiring plastic deformation by the jeweller

Scratch resistant "Magic gold" developed at EPFL