FS 2025/26

MSE-422 – Advanced Metallurgy

9 -The precious metals

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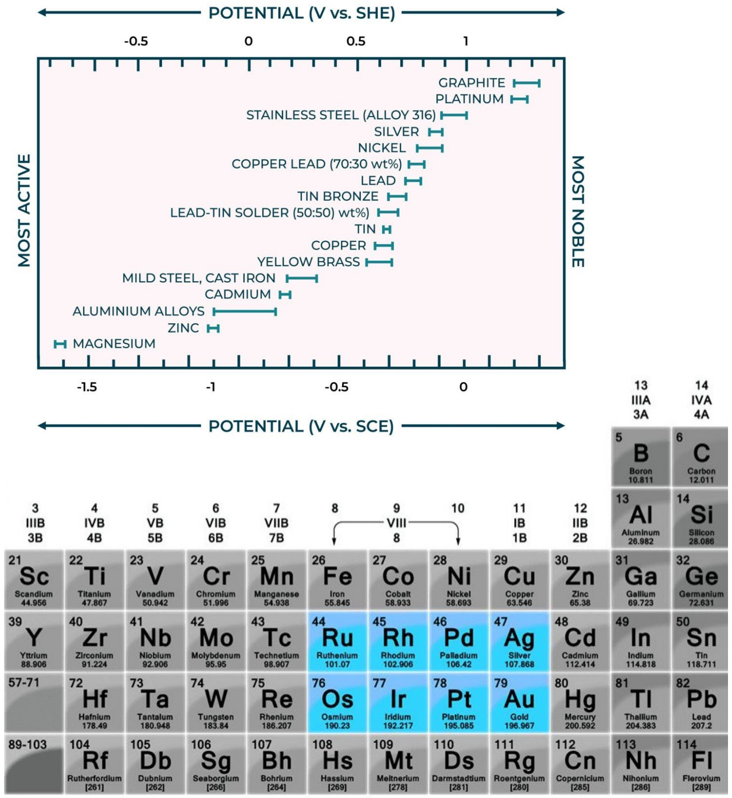
What are precious metals?

- 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.

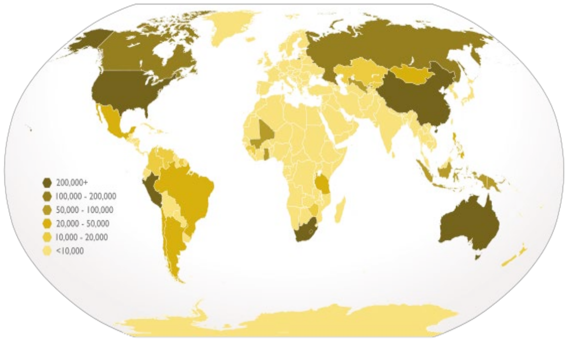


What makes them ‘precious’ or ‘noble’?

- Filled d-bands and high ionization energies
  - Weak tendency to lose electrons; corrosion and oxidation are thermodynamically unfavourable
- Large relativistic effects (Au, Pt, Ir)
  - Contraction and stabilization of the 6s orbital; weakened reactivity
- High cohesive energies and dense atomic packing
  - Exceptional thermodynamic stability and resistance to dissolution
- Low chemical affinity for oxygen, sulphur, halogen
  - Surface remains metallic; oxide layers are unstable or do not form under normal conditions
- Extreme geochemical rarity
  - Low abundance in earth’s crust as they dissolved either in molten metal or in sulphur-rich liquids during planetary differentiation

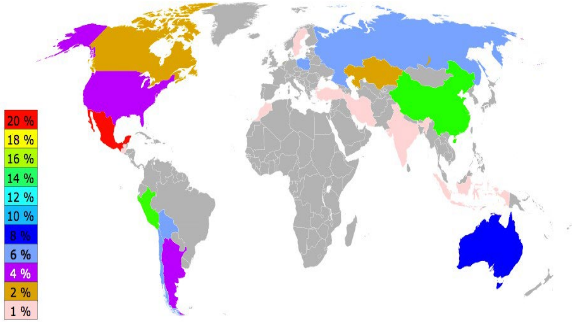
Gold fact sheet

- 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



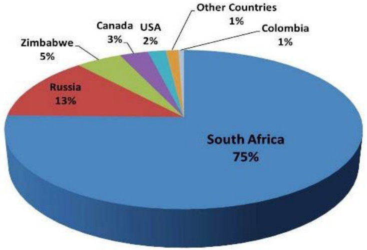
Silver fact sheet

- 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

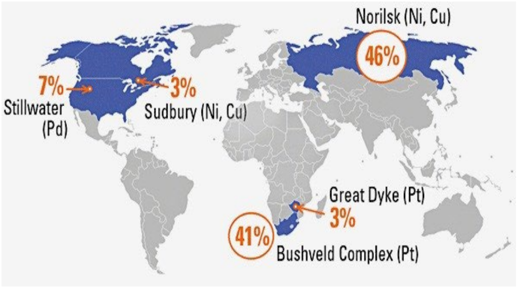

Platinum World Production

Data in kilograms

World Total: 183,000

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 (RuO2), 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

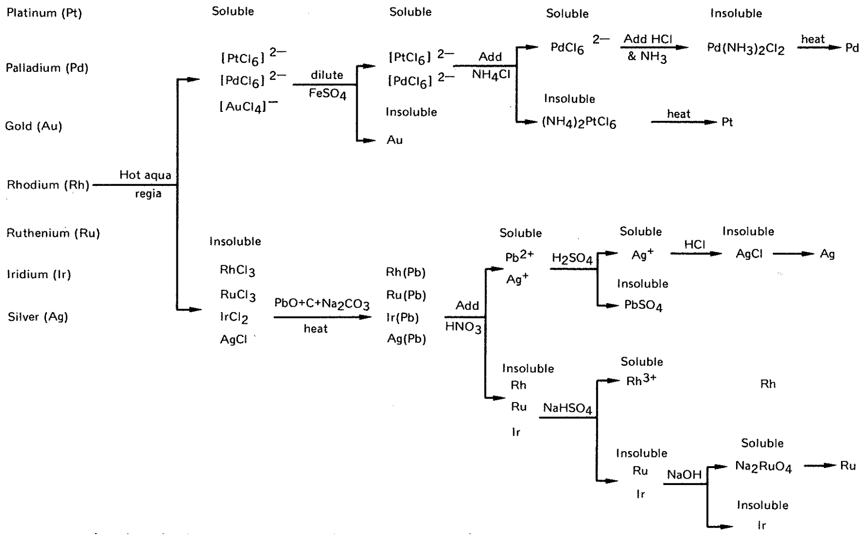
- Occurrence: 0.5 – 1 ppb in earth crust, essentially accompanying Pt resources and Cu and Ni ores
- Reserves: n.a.
- Main producers: South Africa, Russia, US, Canada
- Annual production: 30 t
- Price: 150-170 kUS$/kg (2024)
- Main uses: Catalyst (80% NOx), Jewelry coatings (10%), Chemical industry (10%)
- 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

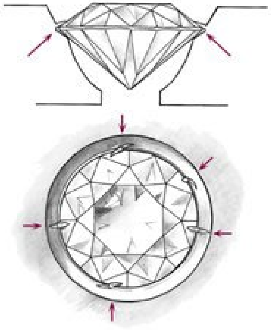
Separation of precious metals

- **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



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)

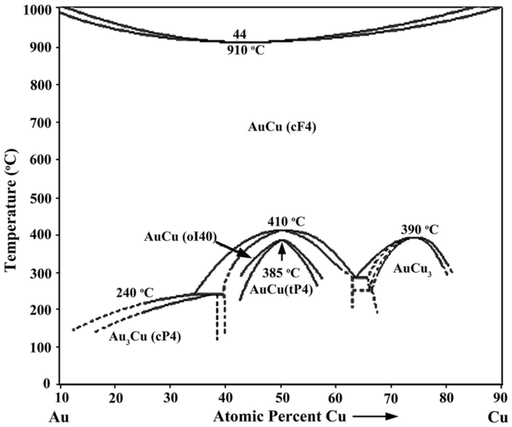


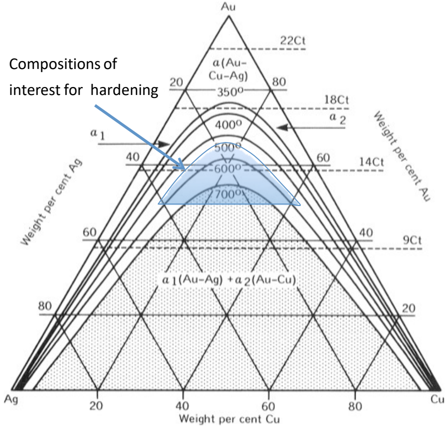
Flush setting requiring plastic deformation by the jeweller

Scratch resistant "Magic gold" developed at EPFL

The metallurgy of gold

- Au alloys are regulated by Hallmarking standards
  - Au content given in parts per thousand, ‰, or in carats, both with regard to the weight
- 1000 ‰ correspond to 24 carats (e.g. a 14 ct gold alloy has 585 wt.- ‰ Au)
- 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
- Role of alloying elements
  - Increase mechanical strength (ss, ppt)
  - Adjust the color

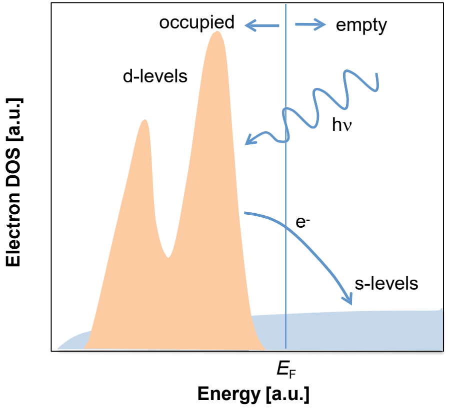


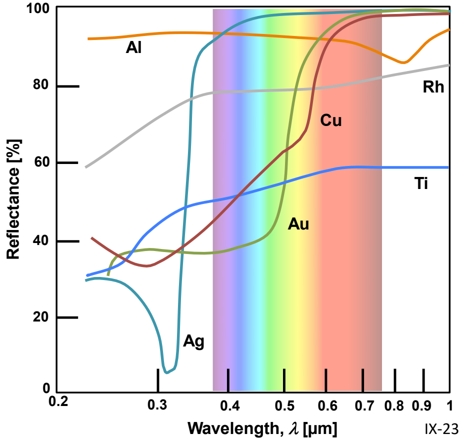


Compositions of interest for hardening

The colors of Au alloys

- The 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 red, 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.





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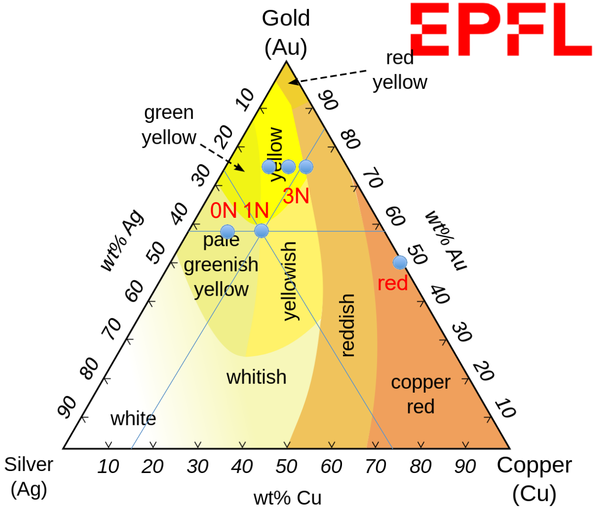
The metallurgy of gold

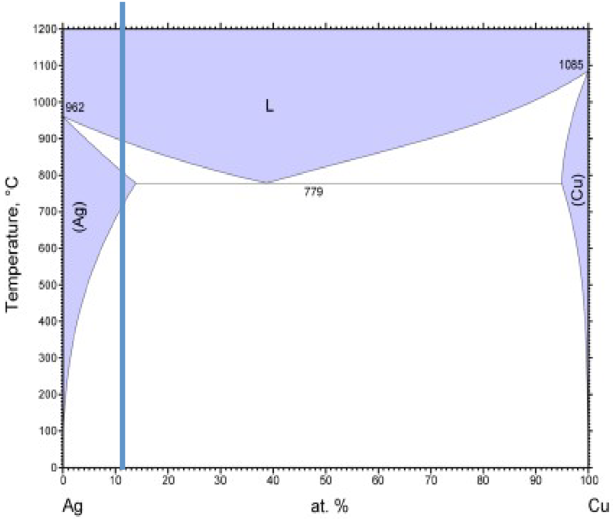
- The color of gold alloys is strongly affected by the composition
  - Ag increases the color changes from yellow to greenish-yellow to white.
  - Cu shifts the color from red-yellow to reddish to copper red
- In order to classify the colors, the N-scale has been developed as comparative scale.
  - 0N 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 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) 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



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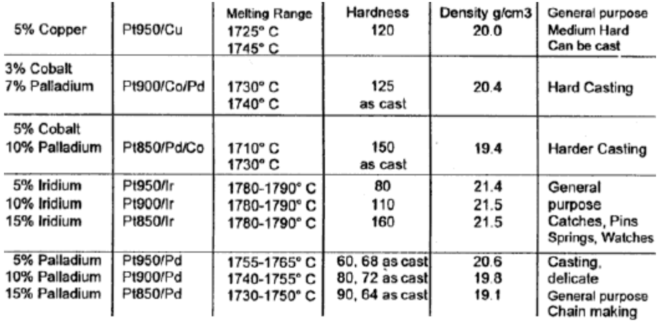
The metallurgy of silver

- Silver oxidizes easily, but Ag_2O becomes unstable above ~200 °C. At high temperature or in the melt, silver dissolves notable amounts of oxygen, which can cause porosity on solidification
- In Ag–Cu alloys, the copper oxide is stable and must be removed after processing
- The main issue for jewelry and silverware is tarnishing (Ag_2S). It can be removed chemically or mechanically
- Rhodium coatings are commonly used to prevent tarnishing and give a bright white appearance.
- Alloying for intrinsic tarnish resistance is preferable; small additions of Ge help, but are not widely adopted industrially.

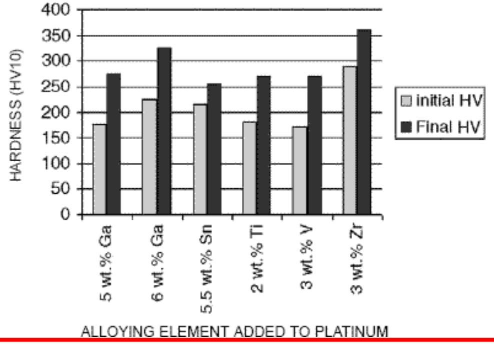
The metallurgy of Platinum

- 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

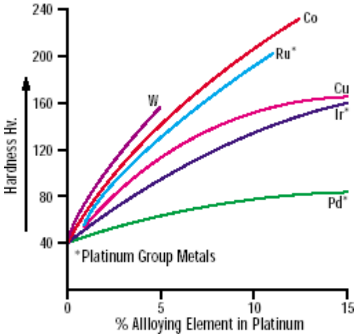


5% Copper	Pt950/Cu	Melting Range 1725° C 1745° C	Hardness 120	Density g/cm3 20.0	General purpose Medium Hard Can be cast
3% Cobalt 7% Palladium	Pt900/Co/Pd	1730° C 1740° C	125 as cast	20.4	Hard Casting
5% Cobalt 10% Palladium	Pt850/Pd/Co	1710° C 1730° C	150 as cast	19.4	Harder Casting
5% Iridium 10% 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



Current research trends - HEAs and BMGs

- Precious-Metal High-Entropy Alloys (HEAs)
  - Focus on multi-component FCC systems based on Pt, Pd, Rh, Ir, Au, Ag
  - Research aims at stable single-phase solid solutions with high strength and good room-temperature ductility (e.g. >30% compression)
  - Challenges include high material cost and predicting phase formation reliably
- Precious-Metal Bulk Metallic Glasses (BMGs)
  - Systems include Au-, Pt- and Pd-based glassy alloys with large supercooled liquid regions (≈40–70 °C) and low T_g, enabling precise thermoplastic forming
  - Attractive combination of very high hardness, elastic limit, and excellent surface quality for jewelry/watchmaking
  - Main drawback: crystallisation during processing → embrittlement, reduced ductility