PRECIOUS METALS

Metallurgy and Related Topics

By

Aldo M. Reti

Topics:

- Metallurgical Aspects
- Gold
  - Karat System
  - Legal Aspects, Hallmarking
  - Color, practical example of *Color Matching*
  - Depletion Gilding, Gold Leaf
  - Gold Filled
- Silver (Ag/Cu System), Reticulation
- Case Study: *Embrittlement of Ancient Silver*
- Platinum (Pt Alloys)

Why "Precious"?

- Expensive, Rare, Desirable
- Noble
- Tradition, History
  - Gold
  - Silver
  - Platinum
  - PGM (Platinum, Palladium, Iridium, Rhodium, Ruthenium, Osmium)
- Usually Alloyed, in order to enhance properties:
  - Mechanical
  - Color
  - "Extend Use"

Gold Alloys

What is Important?

- How much Gold?: Karat System

Karat System (Carat)

- Karat: Gold Content, expressed in 24ths

Karat	Fineness (ppt)
24	1000
22	916.7
18	750
14	583.3
10	416.7
9	375
8	333.3

Gold Alloys

What is Important?

- How much Gold?: Karat System
- Color

Colors of Gold

- Determined by Alloying Elements
- "Classic" System: Au/Cu/Ag (and Zn) is the basis for "Colored Golds"
  - Yellow
  - Red
  - Green
- "White Golds": Au/Cu/Ni or Au/Ag/Pd

  (Ni and Pd are very strong gold "whiteners")

Nickel Allergy

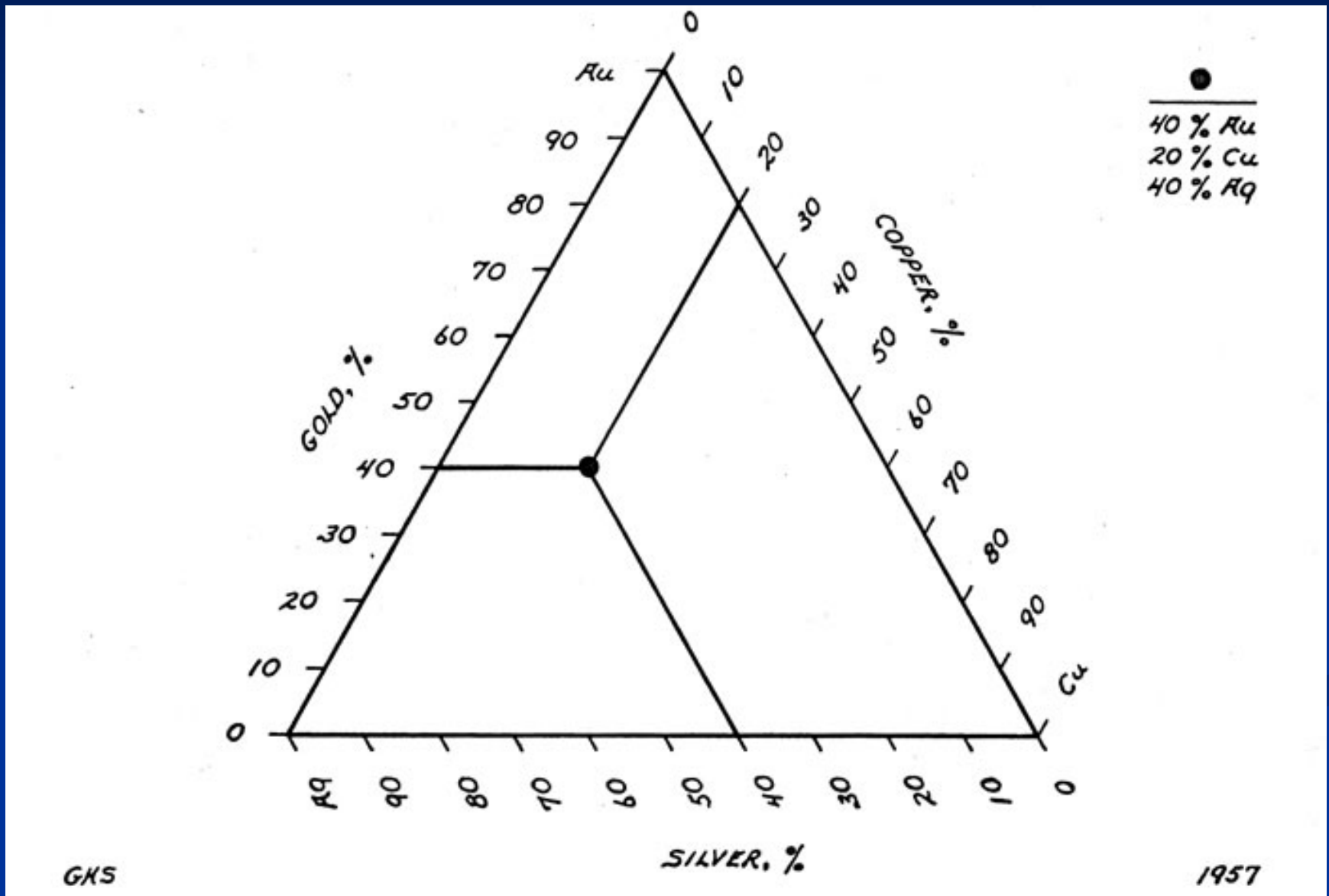
Unfortunately, many people, the female population especially, are allergic to nickel in contact with the skin and this gives rise to a red skin rash or irritation. The European Union countries have enacted legislation valid from the 20th January 2000 that limits nickel release from jewellery. Thus, in Europe, nickel white golds are being phased out and being replaced by palladium white golds. The USA is taking a more relaxed approach, requiring jewellery to be labelled as nickel-containing, and much jewellery in the West is now advertised as 'non-allergenic' or 'nickel-free'. (See article in Gold Technology, No 28, Spring 2000, "Nickel gets under your skin“)

Gold Alloys

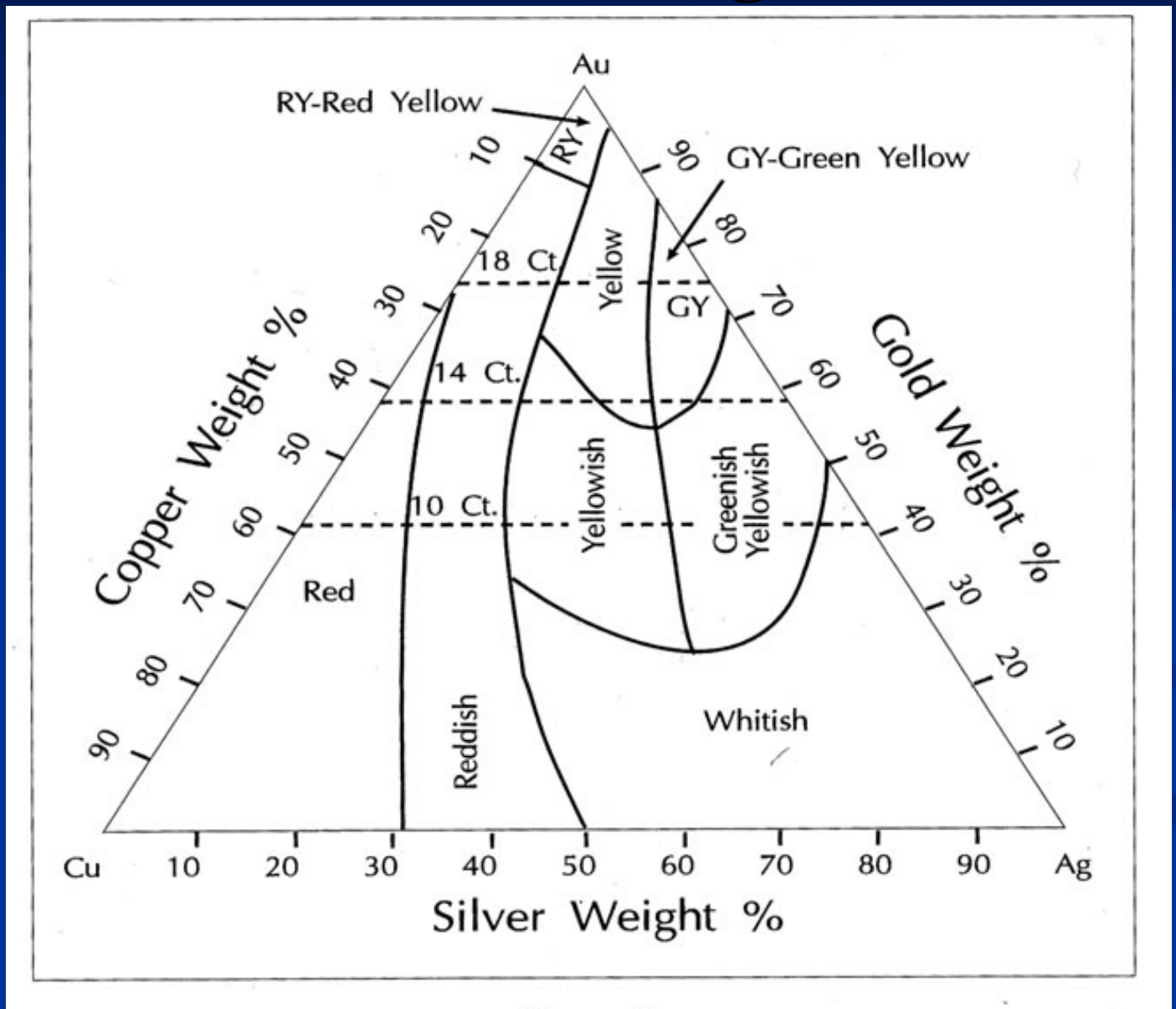
What is Important?

- How much Gold?: Karat System
- Color
- Properties – Utilize Phase Diagrams!
  - Strength, Hardness
  - Working Characteristics
  - Castability (melting point, fluidity)
    - (lost wax process, investment casting)

Ternary Composition Diagram



Gold Color Diagram



Color can be Measured!

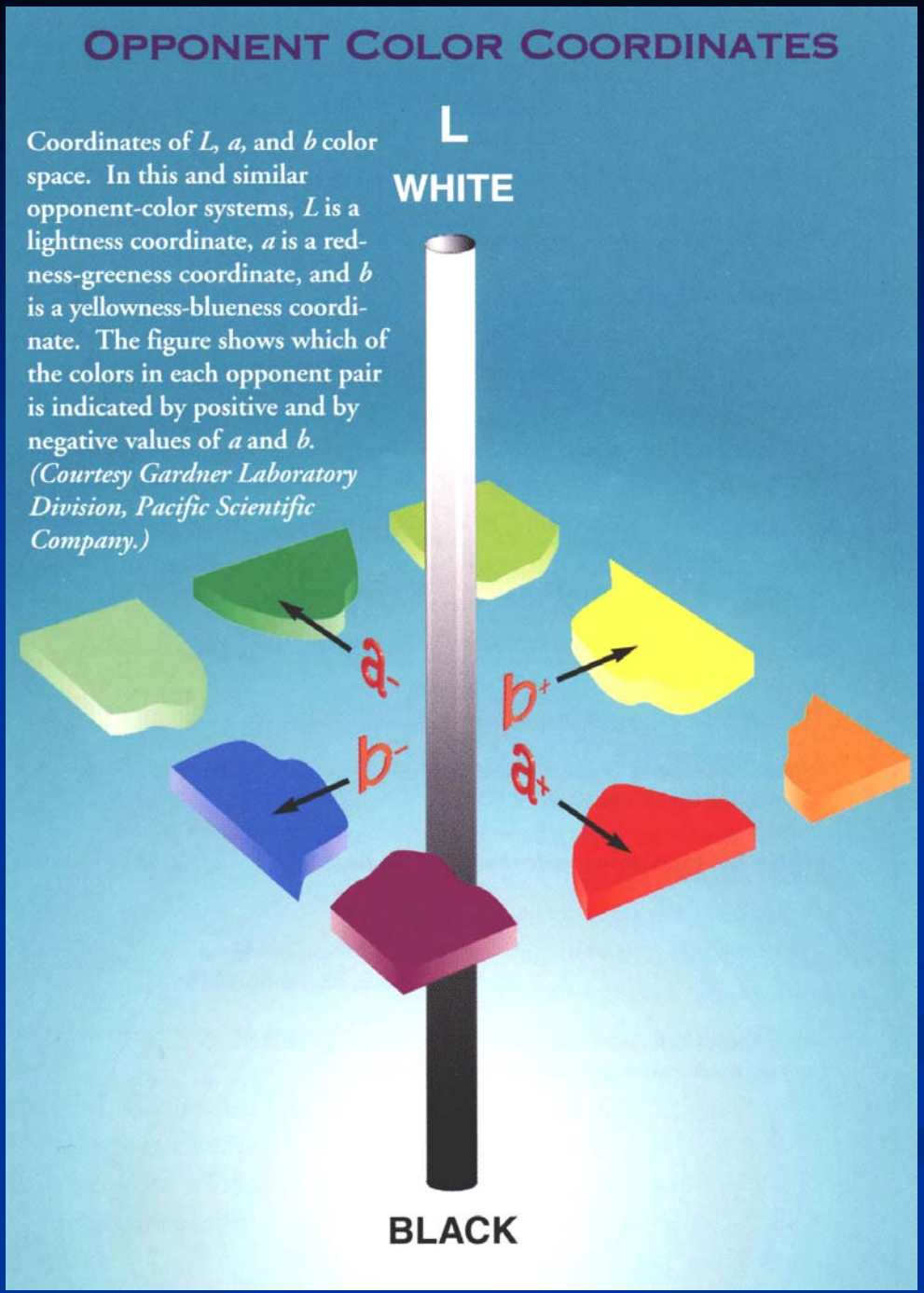
CIELAB Color System

- International System
- Adopted in 1976 by the International Committee on Illumination
- ASTM Standard
- Classic Example of Use: Paint Industry

CIELAB System

- Uses 3 Coordinates:
  - "L" for Brightness (100=white, 0=black)
  - "a" for Red-Green (100=red, -100=green)
  - "b" for Yellow-Blue (100=yellow, -100=blue)
- Thus, Color can be represented by a vector in 3 coordinate space

Opponent Color Coordinates



Coordinates of *L*, *a*, and *b* color space. In this and similar opponent-color systems, *L* is a lightness coordinate, *a* is a redness-greeness coordinate, and *b* is a yellowness-blueness coordinate. The figure shows which of the colors in each opponent pair is indicated by positive and by negative values of *a* and *b*. *(Courtesy Gardner Laboratory Division, Pacific Scientific Company.)*

How to Measure Color?

- Spectrophotometer
- Manufacturers:
  - Macbeth
  - Hunter Laboratories
  - BYK Gardner
  - Applied Color Systems (ACS)

Examples of Color

	L	a	b
Gold	84.0	4.8	34.3
Silver	95.8	-0.7	5.3
Copper	84.0	11.8	14.3
70/30 Brass	91.1	-4.1	22.0

Color Variation in 14 Kt Alloys

Color	Limits a	Limits b
Red	> 3.5	15.0 to 23.0
Yellow	-1.0 to 3.5	18.5 to 23.0
Green	-1.0 to -5.5	17.0 to 23.0
White	-1.0 to 1.0	less than 12.0

Color Difference

Color of metal 1: L_1, a_1, b_1

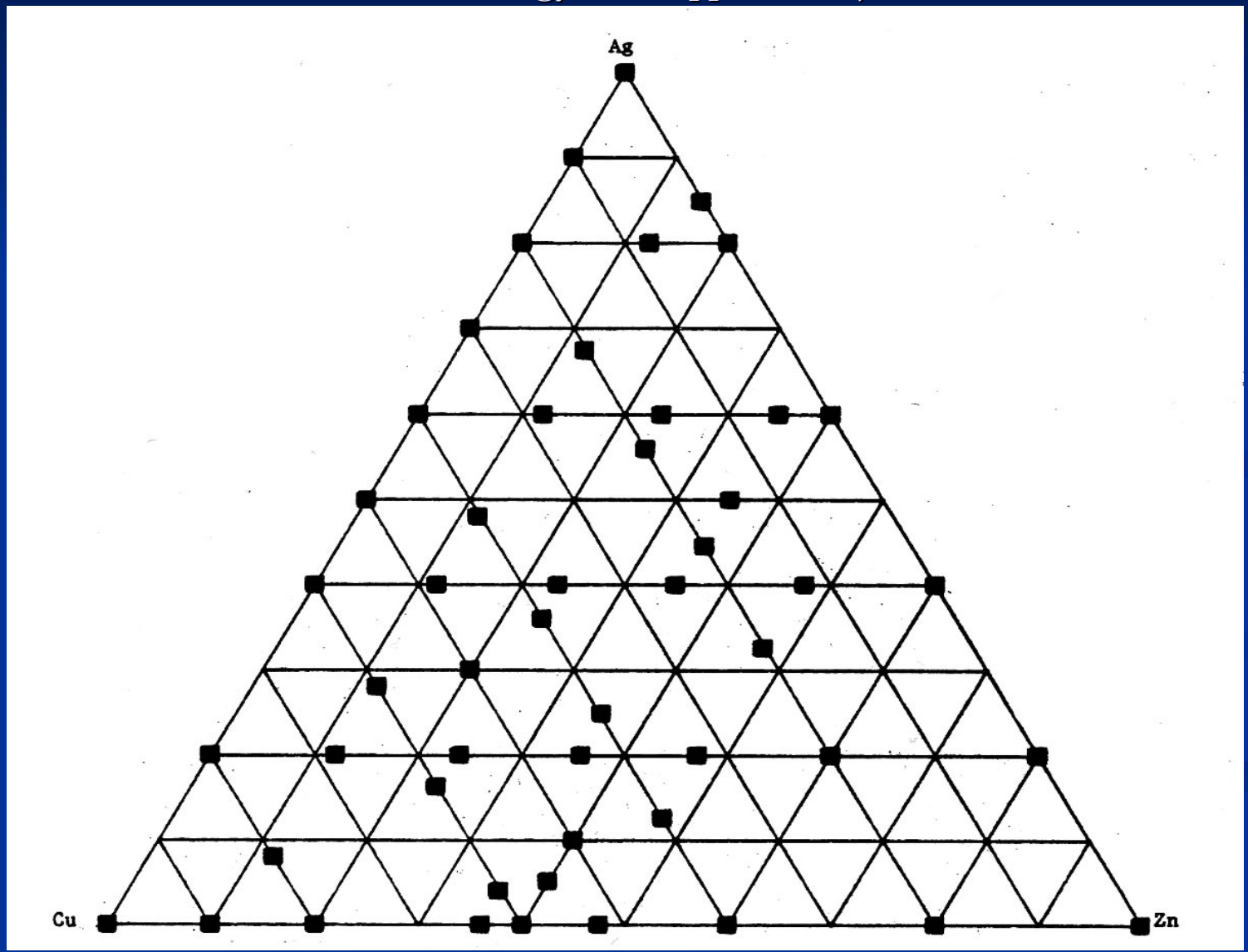
Color of metal 2: L_2, a_2, b_2

$$D^2 = (L_2-L_1)^2 + (a_2-a_1)^2 + (b_2-b_1)^2$$

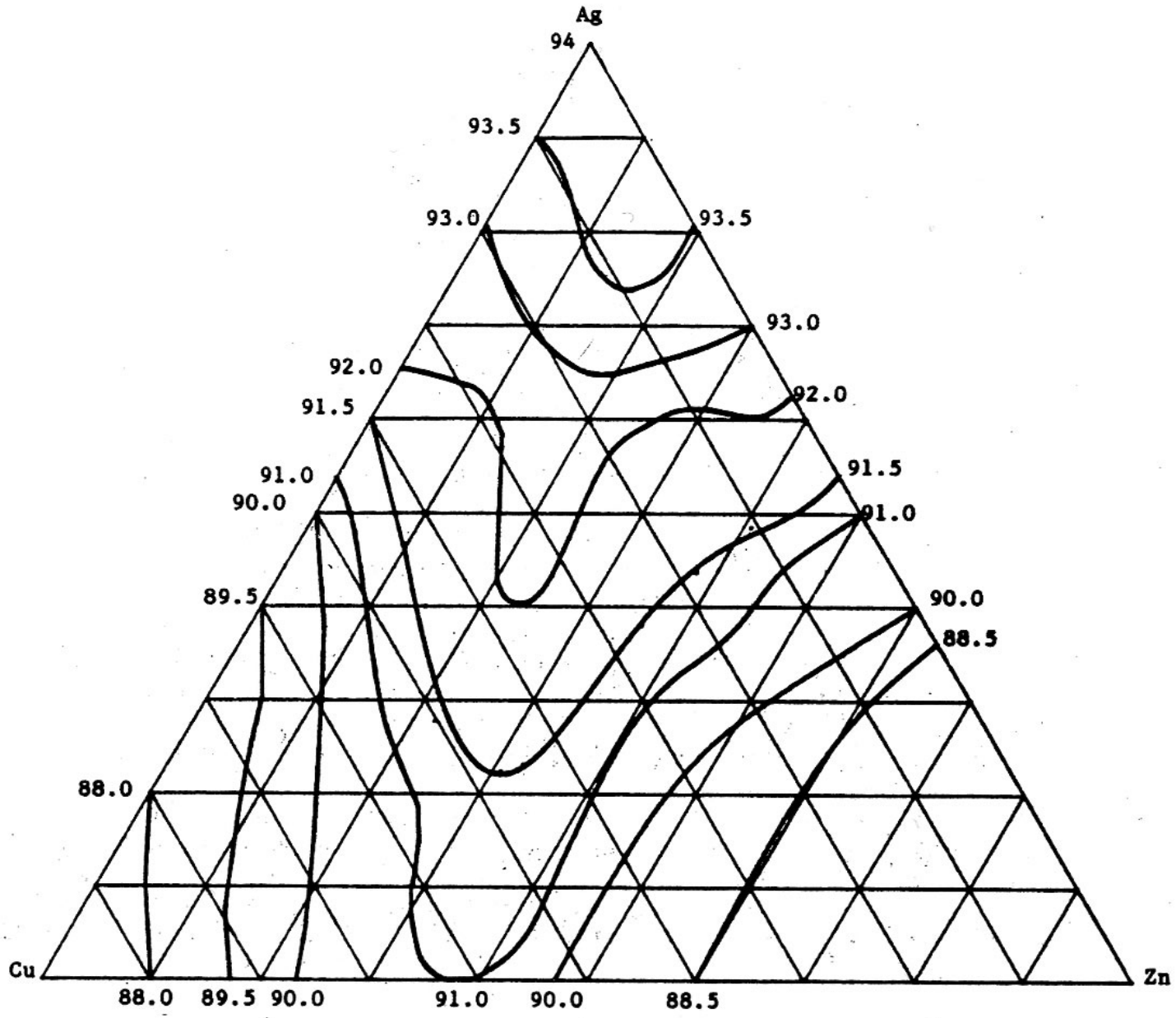
Human eye can differentiate D>2

Composition of 51 14Kt Au/Cu/Ag/Zn Alloys

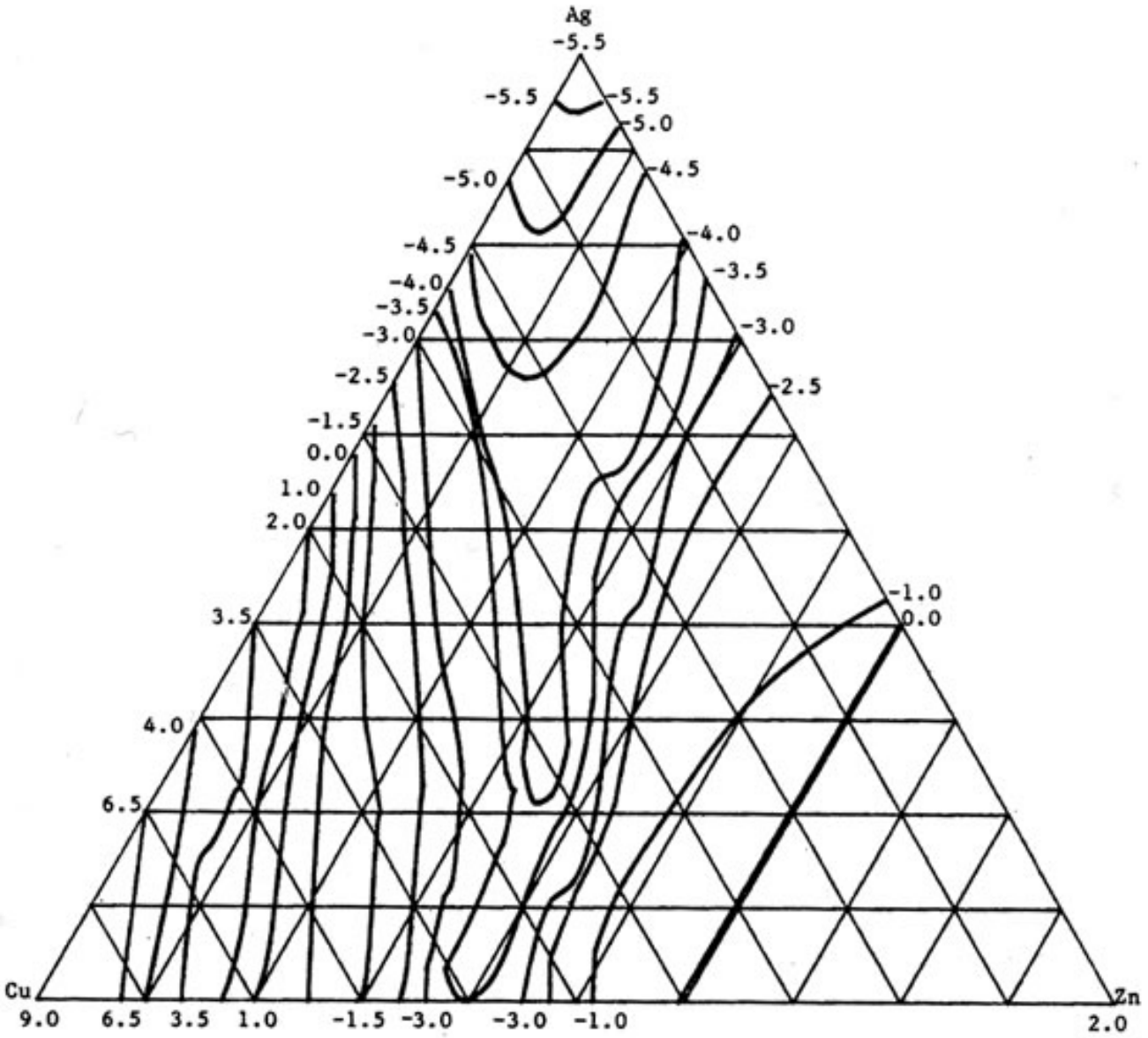
(D.P. Agarwal and G. Raykhtsaum, "The Santa Fe Symposium on Jewelry Manufacturing Technology", 1988, pp. 229-244)



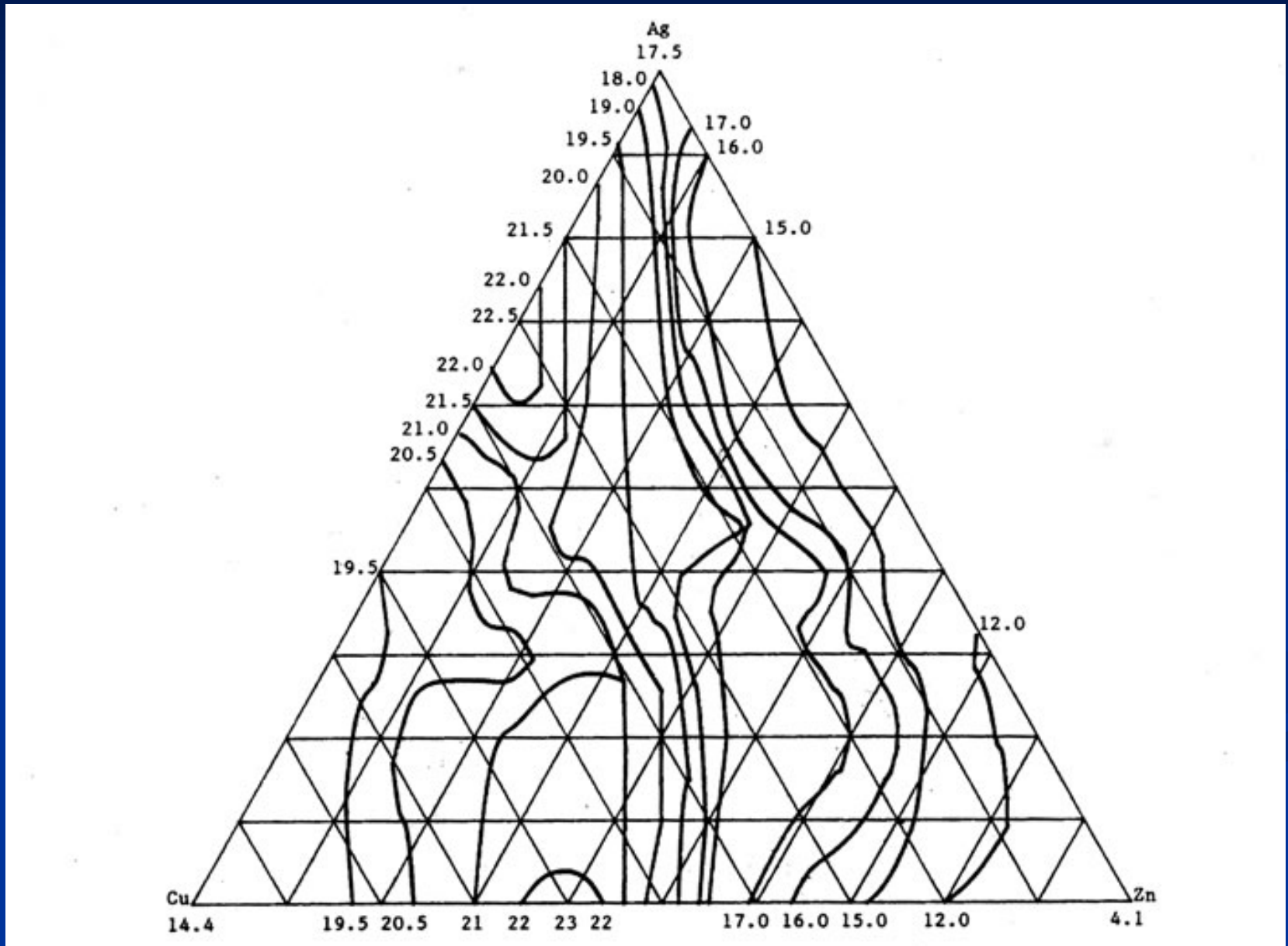
Constant "L" Lines for 14 Kt Au/Cu/Ag/Zn Alloys



Constant "a" Lines for 14 Kt Au/Cu/Ag/Zn Alloys



Constant "b" Lines for 14 Kt Au/Cu/Ag/Zn Alloys



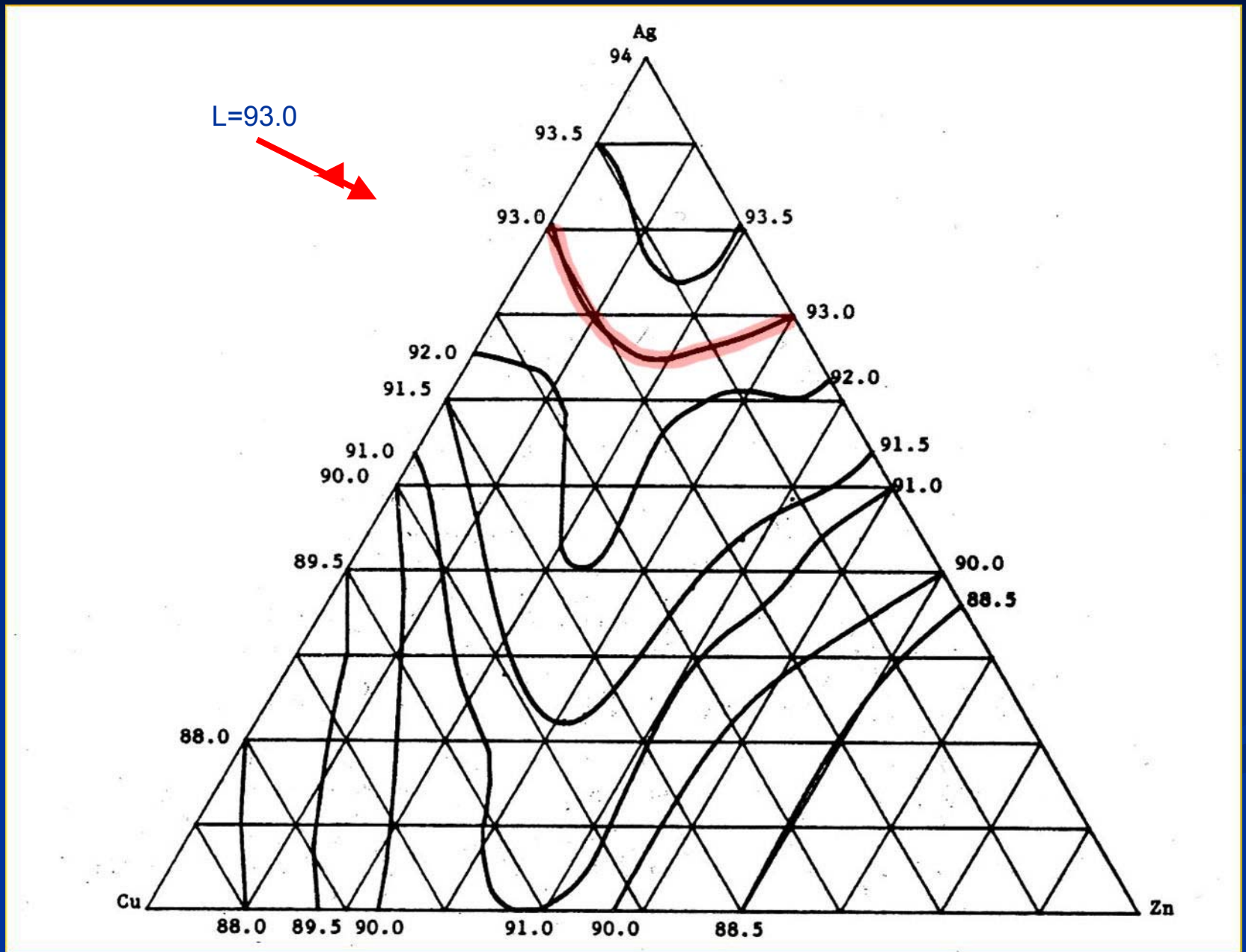
Example of "Color Matching"

- Old piece of gold alloy needs to be matched (repaired) with a new 14Kt alloy
- Measure color of old piece
- Say, L = 93

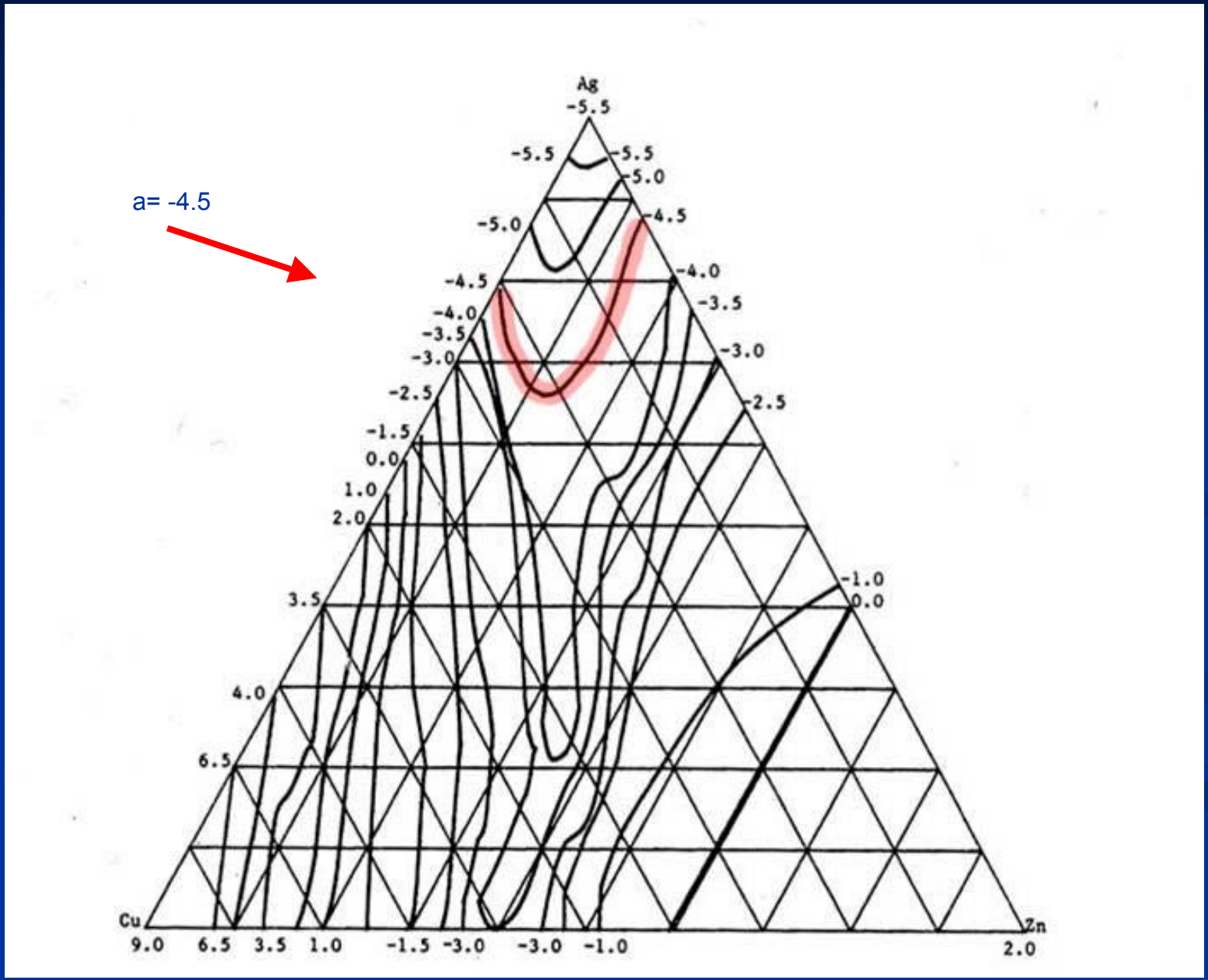
  a = -4.5

  b = 19.5
- Now go to ternary charts to find composition of 14 Kt alloy with best match

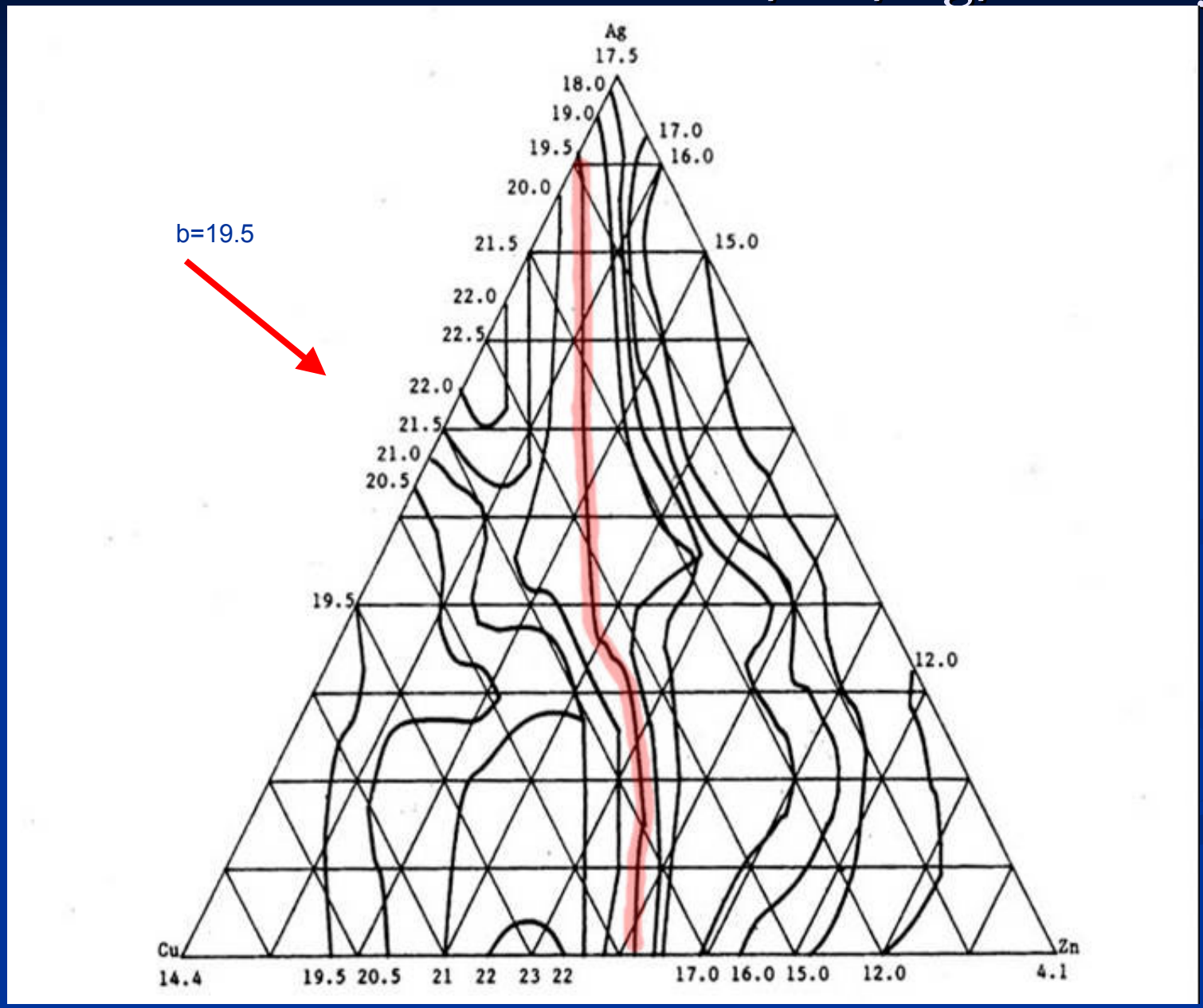
Constant "L" Lines for 14 Kt Au/Cu/Ag/Zn Alloys



Constant "a" Lines for 14 Kt Au/Cu/Ag/Zn Alloys



Constant "b" Lines for 14 Kt Au/Cu/Ag/Zn Alloys

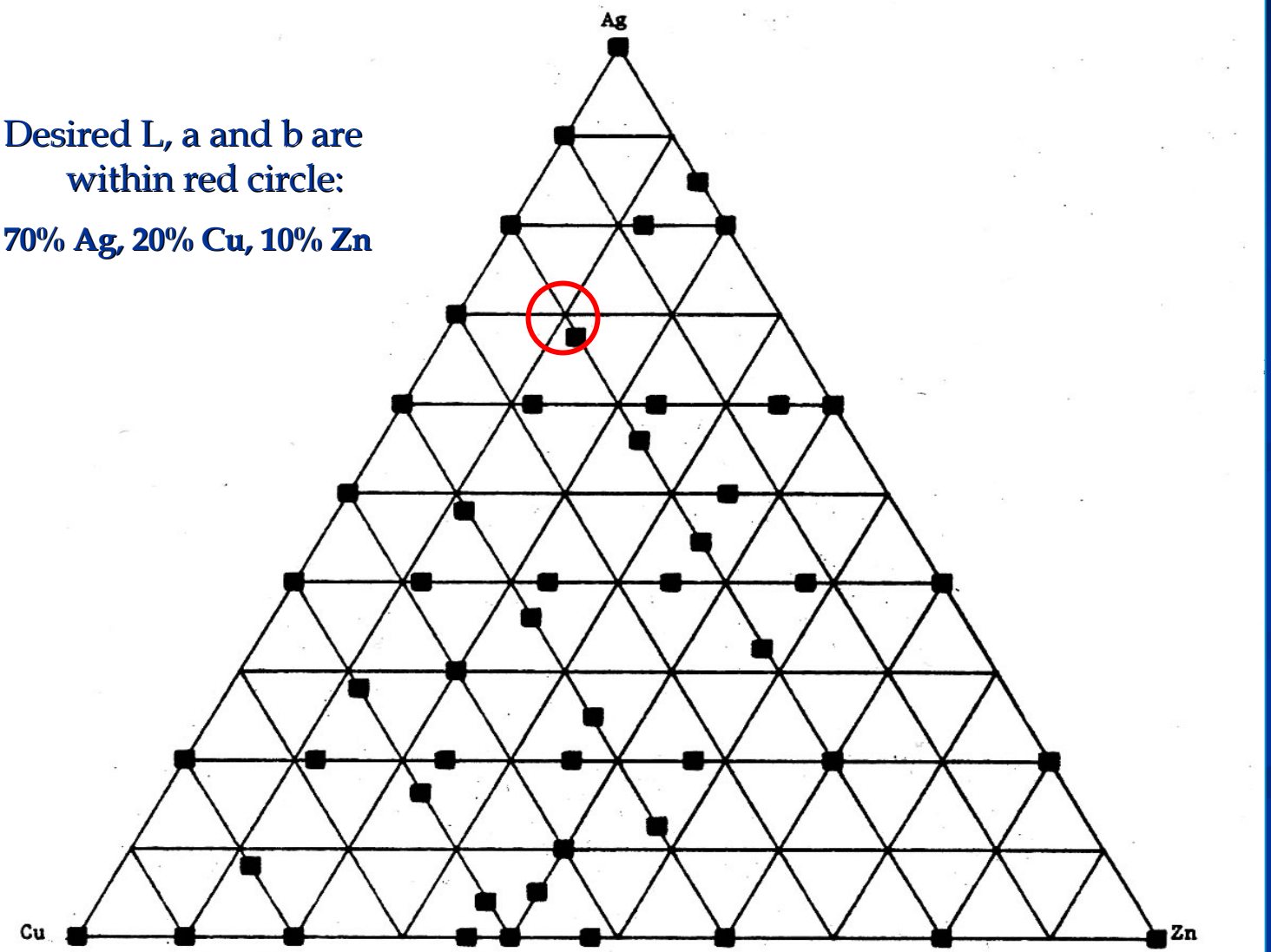


Composition of 51 14Kt Au/Cu/Ag/Zn Alloys

(D.P. Agarwal and G. Raykhtsaum, "The Santa Fe Symposium on Jewelry Manufacturing Technology", 1988, pp. 229-244)

Desired L, a and b are within red circle:

70% Ag, 20% Cu, 10% Zn



Best Color Match 14 Kt Alloy

Silver: 70% x 41.67% = 29.17%

Copper: 20% x 41.67% = 8.33%

Zinc: 10% x 41.67% = 4.17%

Gold: = 58.33%

100.00%

Purple Gold

- **Purple gold (also known as amethyst or violet gold)**
  When gold and aluminium are alloyed in a certain fixed ratio, they form a gold intermetallic compound with the chemical formula $AuAl_2$ (or Au_6Al_{11}). That is one atom of gold to two atoms of aluminium. This compound has an attractive purple color. In terms of composition, this compound is about 79% gold by weight and hence is hallmarkable as 18 carat gold.

- All intermetallic compounds, and purple gold is no exception, tend to be very brittle. They cannot be easily worked by conventional metal working processes. If one attempted to roll or hammer a piece of purple gold, it would shatter into pieces!

- "Purple Plague" when bonding gold wire to aluminum.

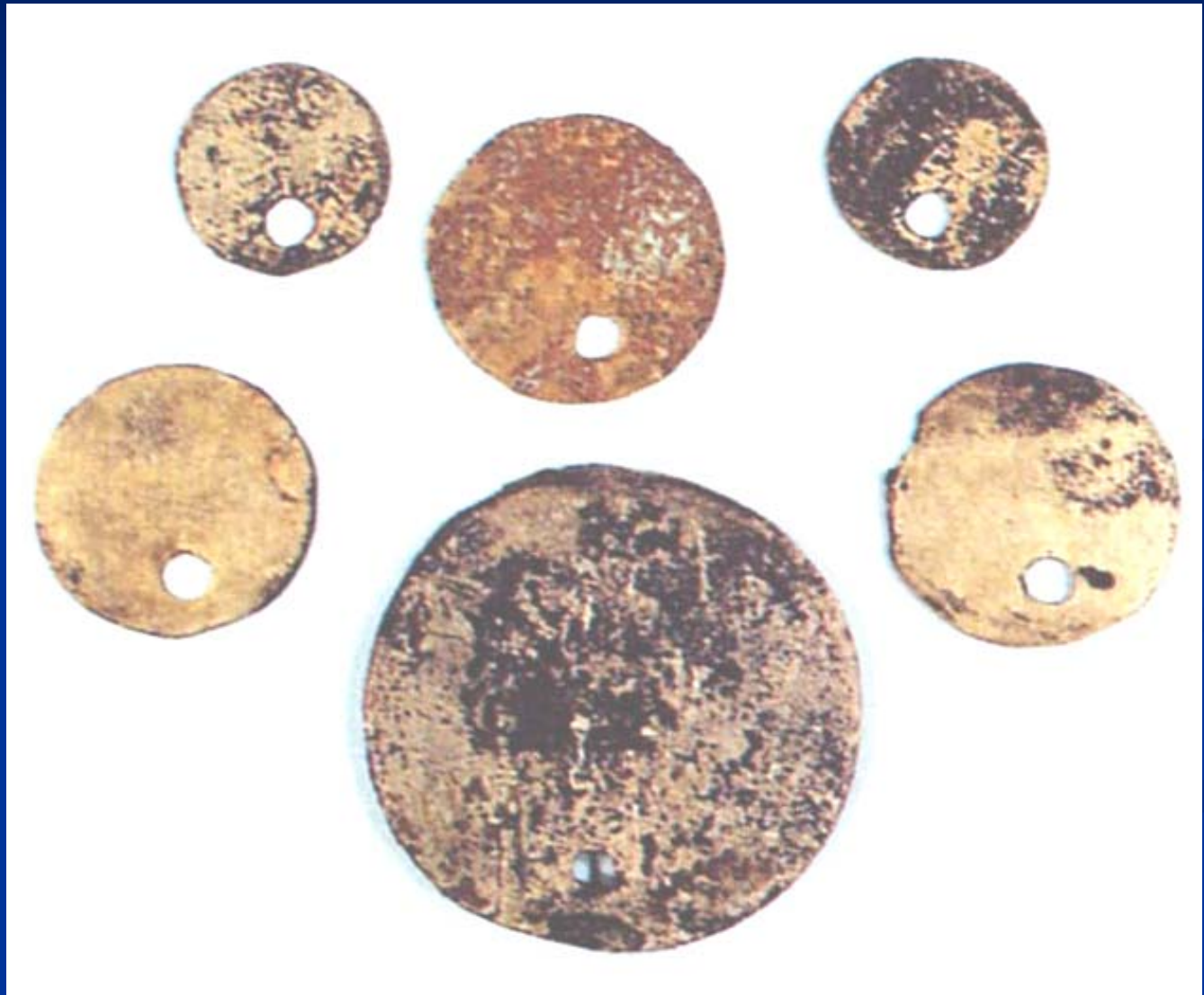
Blue Gold

- Au-Fe Alloys (i.e., 75 Au-25 Fe)
- Au-In Alloys
- Color Interference effect caused by thin film of oxide on surface
- Purple films found in Tutankhamun gold (presence of Fe and As)

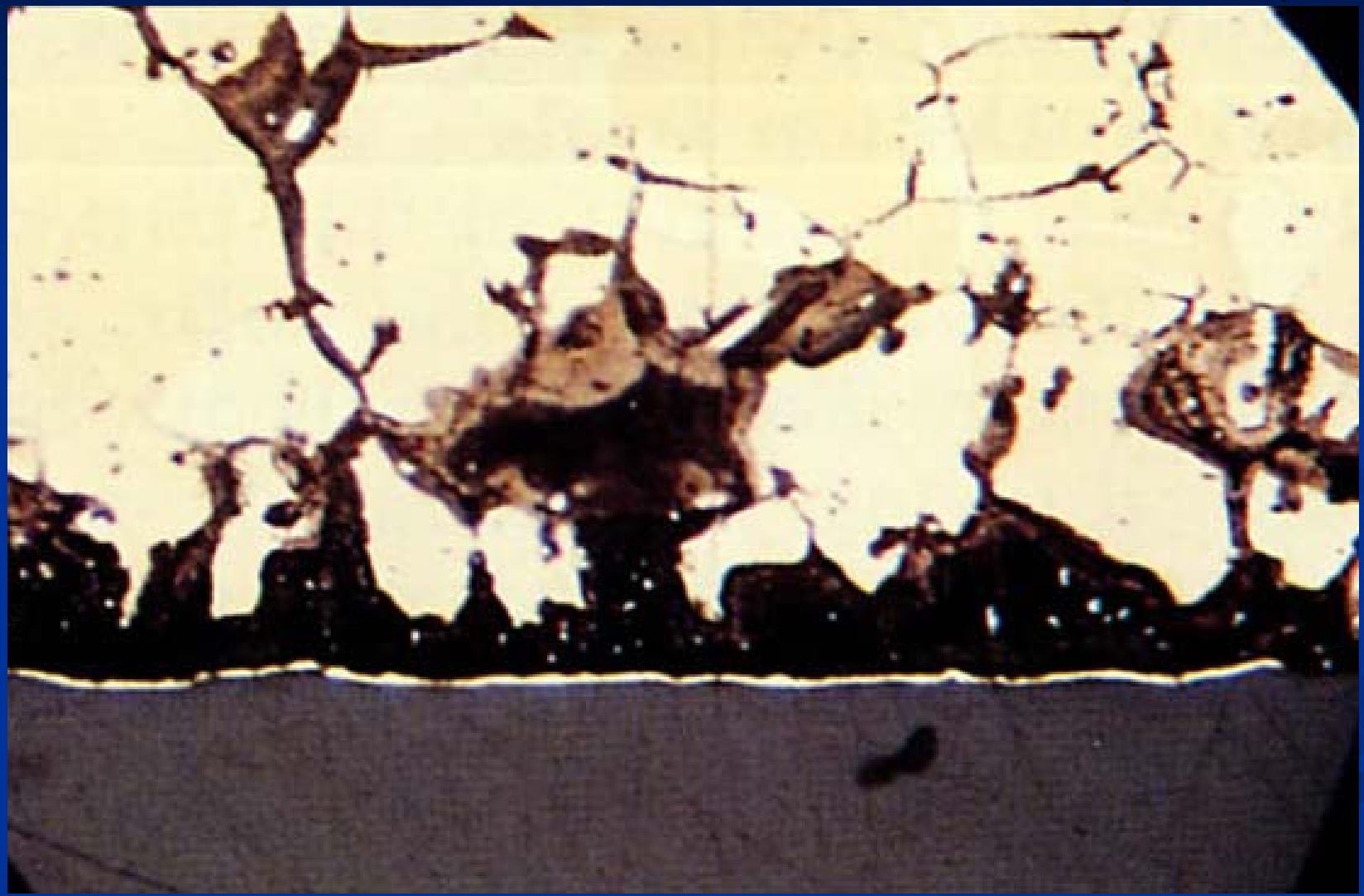
Depletion Gilding

- "Coloring the Gold". Surface rich in gold. Remove base metals from the surface, which is enriched in gold.
- Process: conversion of base metals near the alloy surface:
  - Chemical attack (alum and common salt), applied to *Guanin* (silver-rich). Form silver and copper chlorides, which at high temperature are absorbed by the crucible (cementation)
  - Oxidation/leaching, applied to *Tumbaga* (copper-rich)
- Modern Method: Chemical "Bombing"
  - Hot cyanide solution + hydrogen peroxide

Depletion Gilded Tumbaga from the Vicus Period, Peru



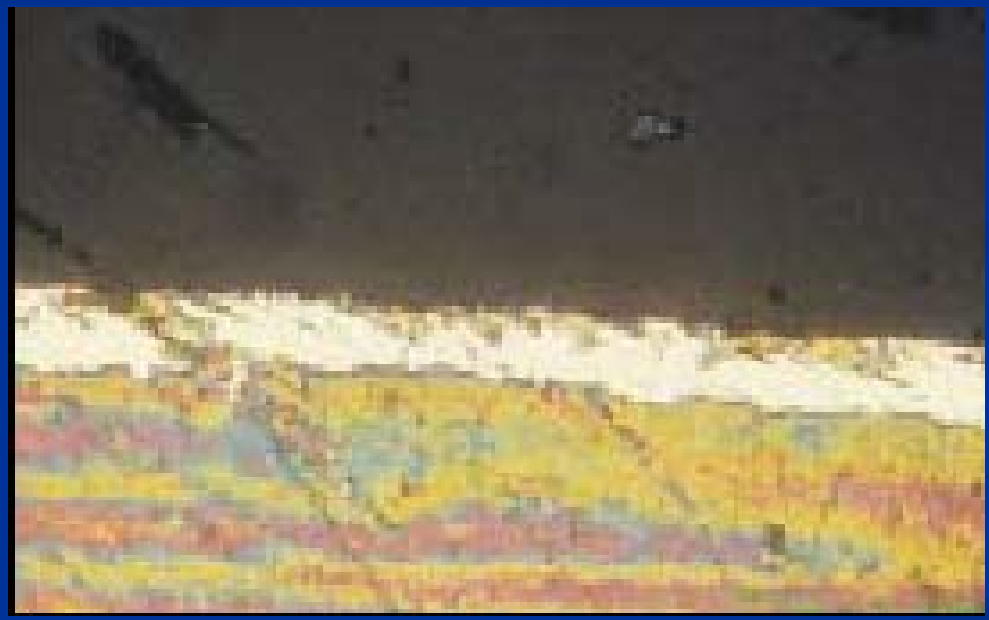
Cross-Section of a Vicus Disc (x200)



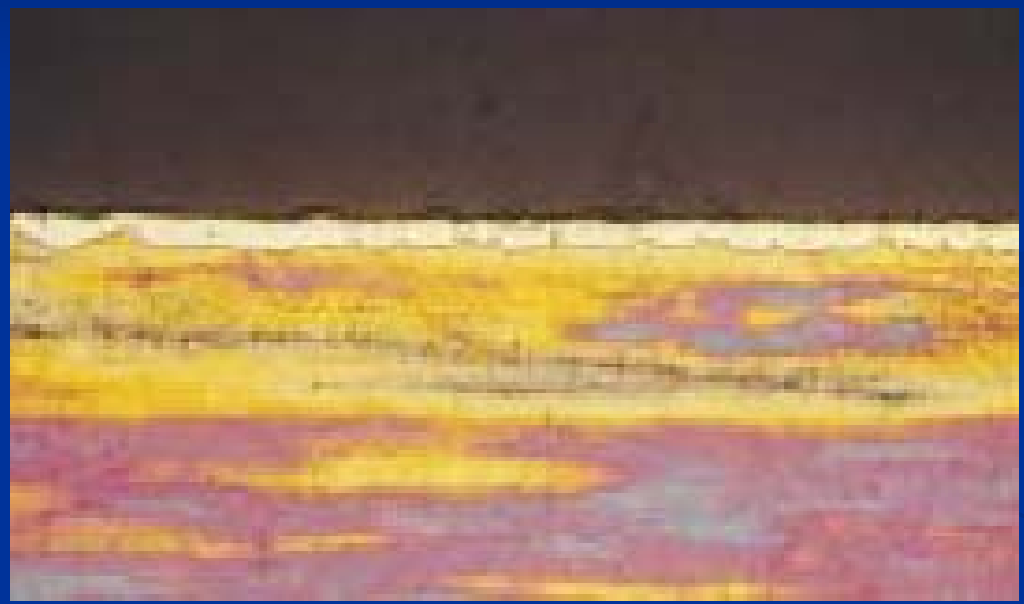
Depletion Gilding

Tribes in Pre-Columbian Peru, specifically the Moche and later the Chimu who were located in northern coastal Peru from between 250 BC to 600 AD and 800 AD to 1500 AD, respectively, hammered copper alloys to make ornamental objects. Pre-Columbian metalsmiths specialized in a copper alloy called *tumbaga*, which is primarily gold and copper, perhaps with some silver because silver typically occurs with gold when found in Andean stream beds. Tumbaga can achieve a gold color, despite being as low as twelve percent gold through a process called **depletion gilding**. Depletion gilding requires pickling a sheet of tumbaga in an acidic solution. Acidic pickling solutions could be easily obtained by the Moche and Chimu by soaking certain plant roots. The pre-Columbian Peruvian's primary interest in metalworking stems from a strong sense of spirituality. They believed that a divine power gave them the ability to "magically" make colors and designs appear in materials from where they had not previously existed, such as bringing a gold color out of a copper colored alloy. One can clearly see how the pre-Columbians would see depletion gilding a copper colored alloy and making it turn gold as a very spiritual activity since they did not understand the metallurgical principles behind depletion gilding.

9 Kt Gold-Silver Alloy treated 7 hours at 165 C in alum paste (x250)



9 Kt Gold-Silver-Copper Alloy after 9 cycles of torch heating in alum paste (x400)



Gold Leaf

- Few millionths of an inch thick (about 1/10 micrometers)
- Dates back….5,000 years?.... 1352 B.C., King Tutankhamun
- Mechanical method, no heat. Two dimensional tensional stresses and compression in the third direction
- Gold with ~ 4% Silver. Also, some Copper (all have same crystal structure)
- Formation of new "sub-grains" as the gold alloy is worked
- Decorative uses, resistance to corrosion. Domes, altars, printing, buildings

Beating technique: *Gold is first rolled into ribbons 1/1,000" thick, then cut into 1 1/4" squares and placed in squares of seaweed paper, encased in turn in parchment paper. This packet, called a "cutch", is then squeezed in a press to compress the paper. The "cutch" is then beaten with a 17 lb hammer until the gold is in 4 inch squares. These are then placed in ox skins, coated with brime, a powder-like substance made from volcanic ash, brushed on with the hind leg of a Russian hare. This new packet, a "shoder" is beaten for 2 hours with a 9 lb hammer, then divided again into a "mould" wrapped in parchment paper, which is beaten with a 7 lb hammer. In all, about 82,800 blows are necessary to reduce the gold to 3 millionths of an inch in thickness. The gold is then so delicate that it can be cut only with a malacca reed shaped into a cutting tool or "wagon" which is slid across the gold.* (From: *The Gold Companion*, by Timothy Green).

Corrosion of Gold

- Does Gold Tarnish?
- Tarnish: discoloration of metal surface caused by a thin layer of a reaction product (oxide or sulphide)
- Karat dependent, i.e., 14 Kt contains ~ 30 to 35 volume percent gold, the rest are base metals
- Agents: perspiration, food, perfumes, household cleaners, etc. Also, solders are sometimes of lower karat

RESOURCES

- World Gold Council www.gold.org
  - Gold Technology
  - Gold Bulletin
- MJSA www.mjsainc.com
  - AJM Magazine www.ajm-magazine.com
  - Annual Trade Show
- The Santa Fe Symposium on Jewelry Manufacturing Technology www.santafesymposium.org
- International Precious Metals Institute www.ipmi.org
- Hallmarking Office www.theassayoffice.co.uk
- Federal Trade Commission www.ftc.gov
- The Silver Institute www.silverinstitute.org
- Platinum Metals Review www.platinummetalsreview.com
- Platinum Guild International www.pgi-platinum-tech.com
- FEM (Institute for Precious Metals, Germany) www.fem-online.de
- Books:

W.S. Rapson, "Gold Usage", Academic Press (1978)

A. Butts and C.D Coxe, "Silver, Economics, Metallurgy and Use", Van Nostrand (1967)

T. Green, "The Gold Companion", Rosendale Press Ltd. (1991)

Resources (Cont.)

- Materials and Supplies:

  Conservation Resources International LLC
  http://www.conservationresources.com/Main/S%20CATALOG/CoverPage.htm

- For Gold Products:
  http://www.utilisegold.com/

Another Resource

- **©The American Institute for Conservation of Historic & Artistic Works**

  1717 K Street NW, Suite 200
  Washington, DC 20036-5346
  202-452-9545
  202-452-9328 (fax)
  http://aic.stanford.edu/about/index.html

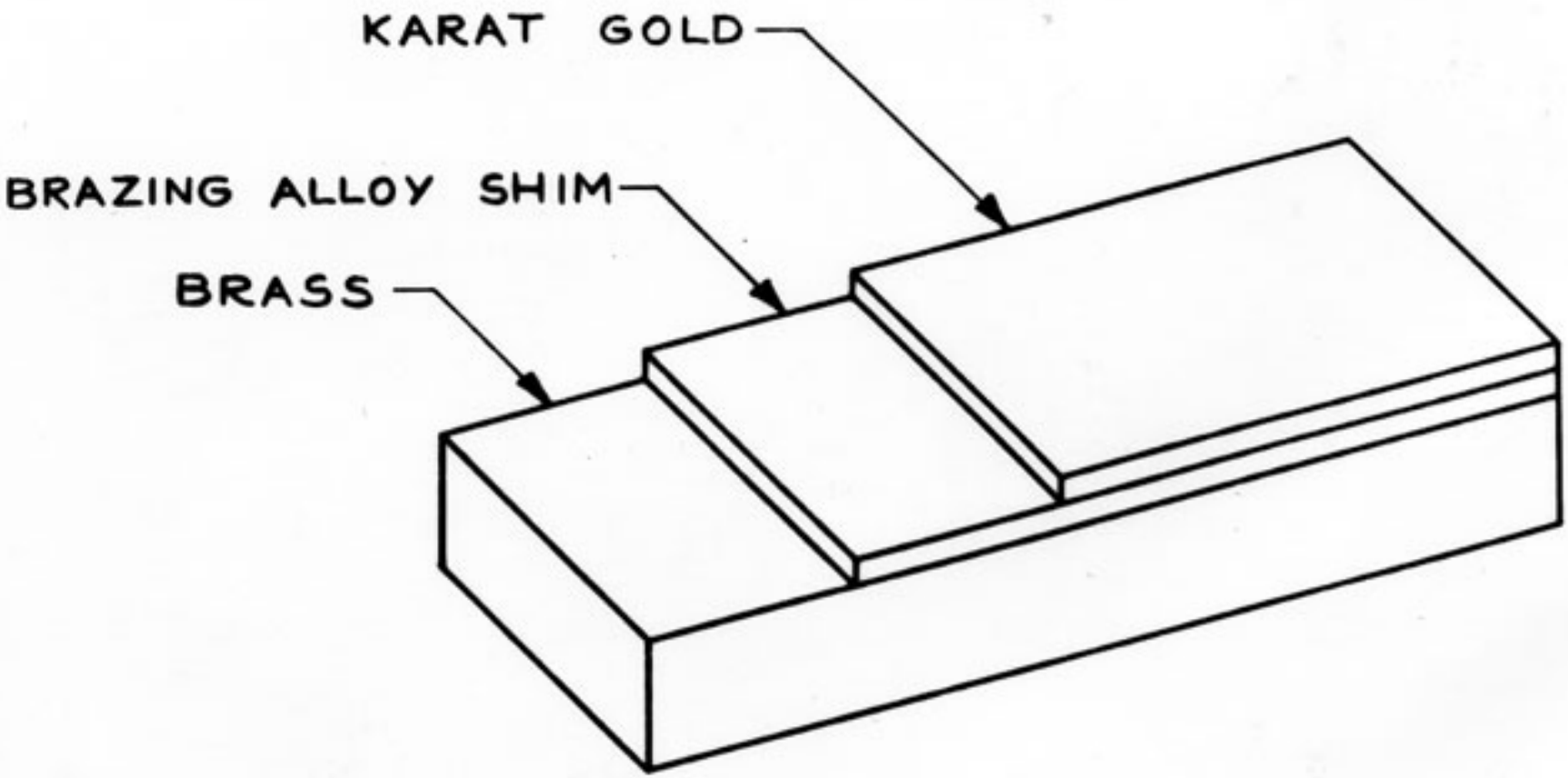
The American Institute for Conservation of Historic and Artistic Works (AIC) is the national membership organization of conservation professionals dedicated to preserving the art and historic artifacts of our cultural heritage for future generations.

Gold Filled

- Is it *filled with gold?*
- Early applications, wrapping gold around a metal rod, fusing it and drawn into wire, thus: *"gold, filled with base metal"*

How is G.F. or R.G.P. Made?

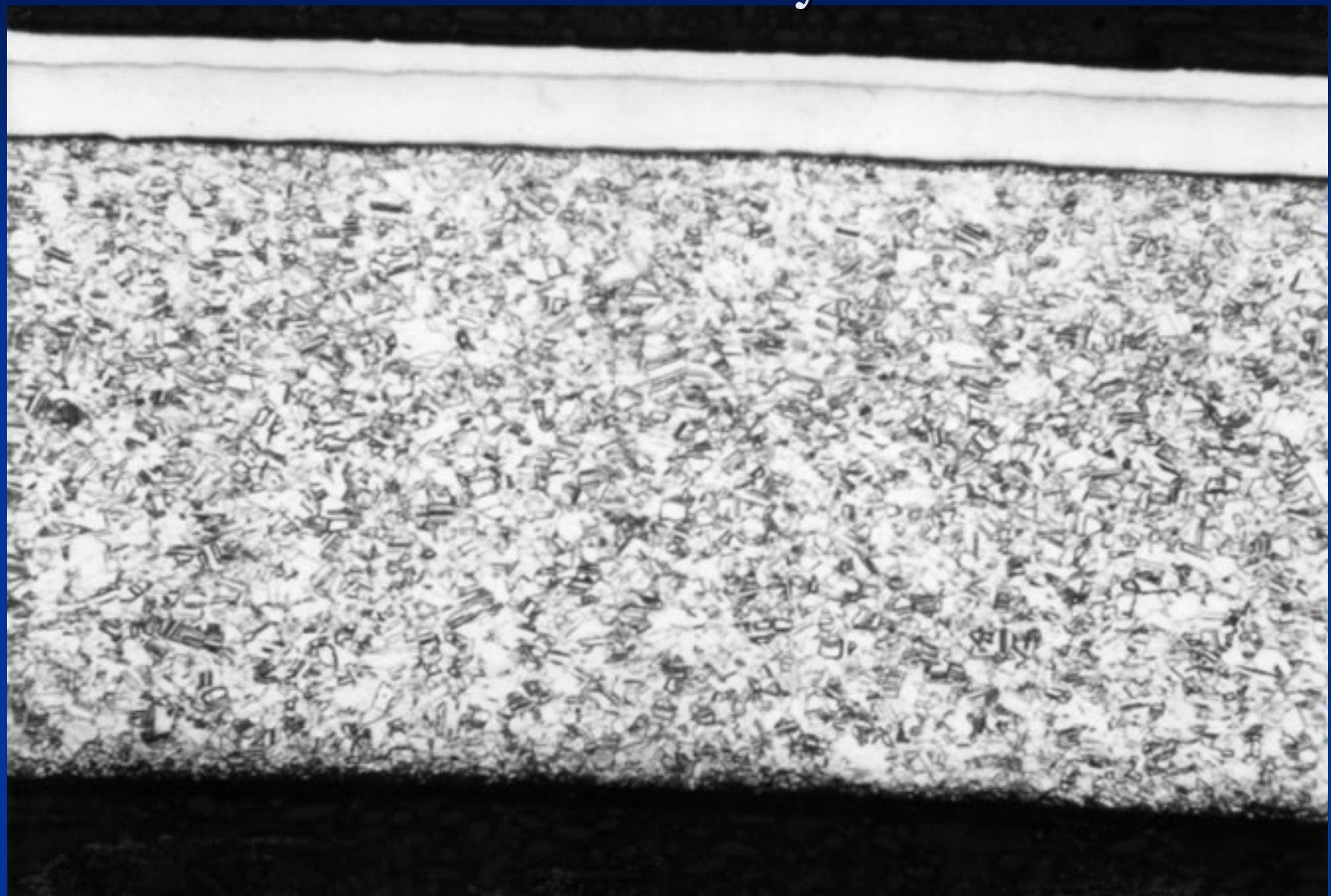
Components for Gold Filled Sheet



18 Kt Gold on Brass

1/56 10 Kt Gold on Nickel

1/20 14 Kt Gold on Phosphor Bronze with a Nickel Interlayer



Gold Filled Wire

- How is it manufactured?
- Start by making a plate…….

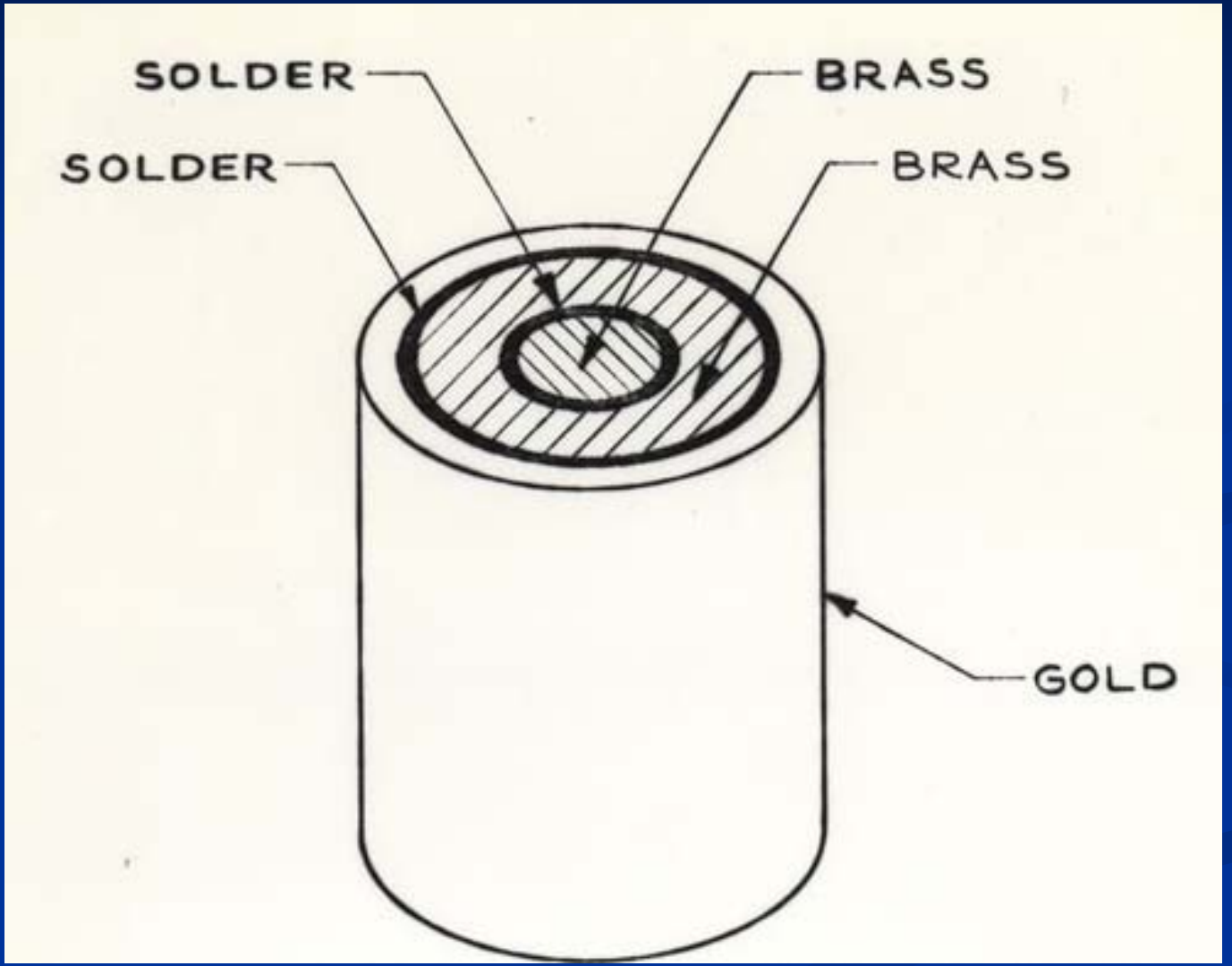
Karat Gold, Brazing Alloy and Base Metal Disk Components (Top: after brazing)

Left to Right: Bonded Disk, Rolled into Circle, Cut Circle

Deep-Drawn Cups (Gold Surface Outside)

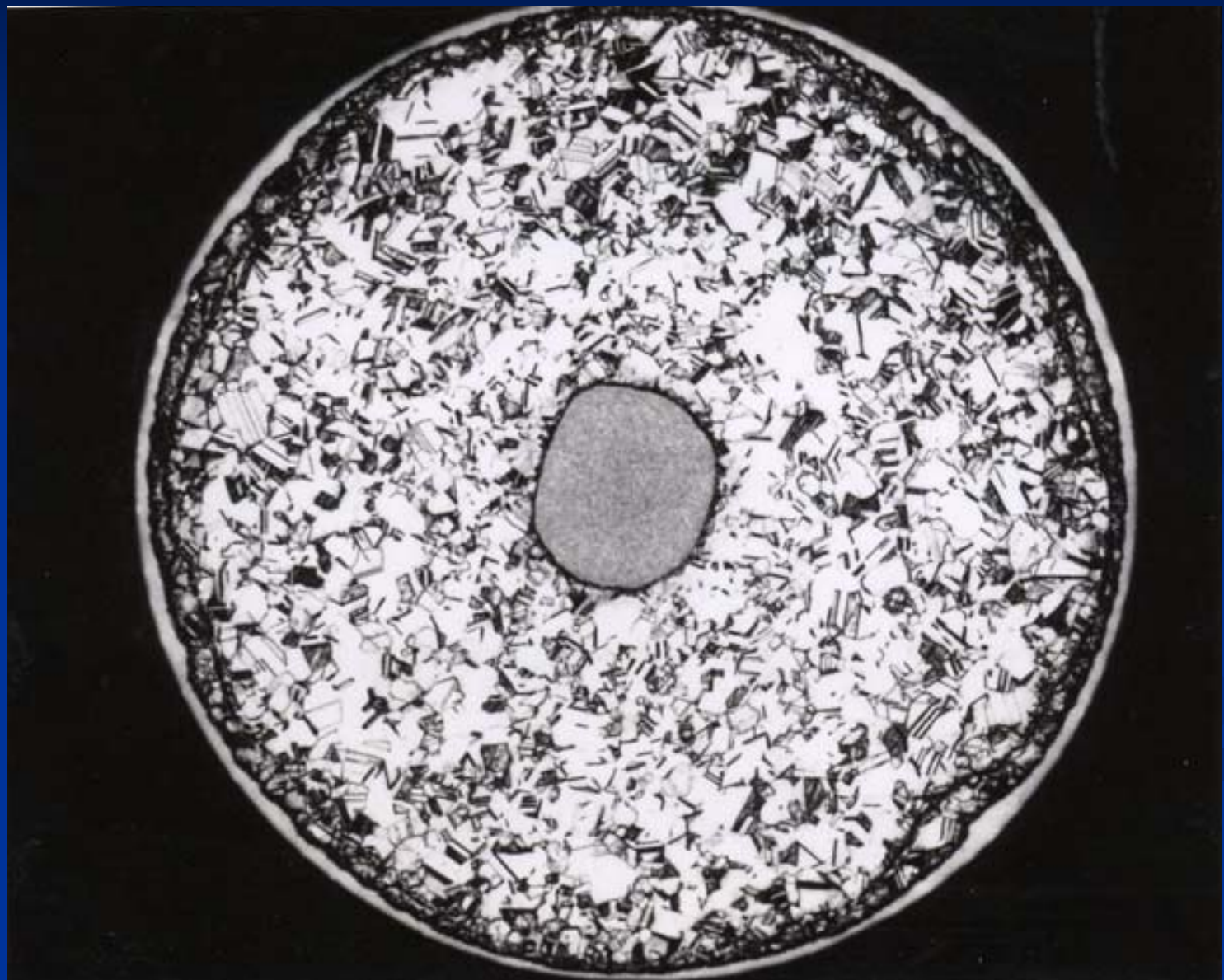
Stages of Deep Drawing

Components of Gold Filled Wire



Bracelets made from Gold Filled Pattern Wire

Gold Filled, Solder Core Wire



Gold Filled, Solder Core Wire with a Nickel Interlayer

Intrinsic Value

14 Karat Gold: 14/24 x 600 = $ 350/oz

1/20 14 Kt G.F.: 1/20 x 14/24 x 600 = $ 17.50/oz

1/20 12 Kt G.F.: 1/20 x 12/24 x 600 = $ 15.00/oz

U.S. Regulations for the Jewelry Industry

- National Gold and Silver Stamping Act (amended in 1976 with the Gold Labeling Act)
- Federal Trade Commission Guides for the Jewelry Industry (1997 revision), these guides cover industry products made of precious metals, diamonds, pearls, gemstones, watchcases and watchbands

FTC Guides

- Gold: minimum 10 Kt, 3 ppt tolerance
- Silver, Solid Silver, Sterling Silver:

  At least 92.5% Ag (925/1000)
- Coin Silver, 90.0% Ag (900/1000)
- Nickel Silver (German Silver)?

Gold Filled

- *A product on which there has been affixed a plating of gold alloy of not less than 10 Kt fineness*
- *Plating must be at least 1/20 of the weight of the entire article*
- *Plating must be affixed by mechanical means such as soldering, brazing, welding*

Marking for Gold Filled

14 Kt Gold Filled

14 Kt G.F.

14 Kt Gold Plate (d)

14 Kt Gold Overlay

14 Kt R.G.P.

Rolled Gold Plate, Gold Plate, Gold Overlay

- Same as Gold Filled, *except* the specified 1/20th by weight
- Strict marking requirements:

  1/40 12 Kt Gold Plate

  1/40 12 Kt R.G.P.

  1/40 12 Kt Gold Overlay
- Cannot call it Gold Filled unless the plating is at least 1/20th by weight

Gold Electroplate

- Affix gold by electrolytic process
- No less than 10 Kt
- Minimum thickness equivalent to 7 millionths of an inch (0.18 micrometers) of fine gold

Heavy Gold Electroplate

- As before, except coating with minimum thickness 100 millionths of an inch (2.5 micrometers)

Vermeil

- Base: Sterling Silver
- Minimum gold thickness: 120 millionths of an inch (3 micrometers)
- Gold coating either mechanical or electroplated

Gold Flashed, Gold Washed

- 10 Kt minimum
- No minimum coating thickness requirement

Quality Marking

- Trademark: name or trademark of the manufacturer, importer, or seller
- Place trademark adjacent to quality mark
- However……. System is difficult to police! And in the U.S. no Independent Assaying is Required

COUNTRIES WITH AN INDEPENDENT HALLMARKING SYSTEM

Austria
Cyprus
Czech Republic
Denmark
Finland
France
Hong Kong
Ireland
Malaysia
United Kingdom
Netherlands
Norway
Portugal
Singapore
Spain
Sweden
Switzerland
Uzbekistan

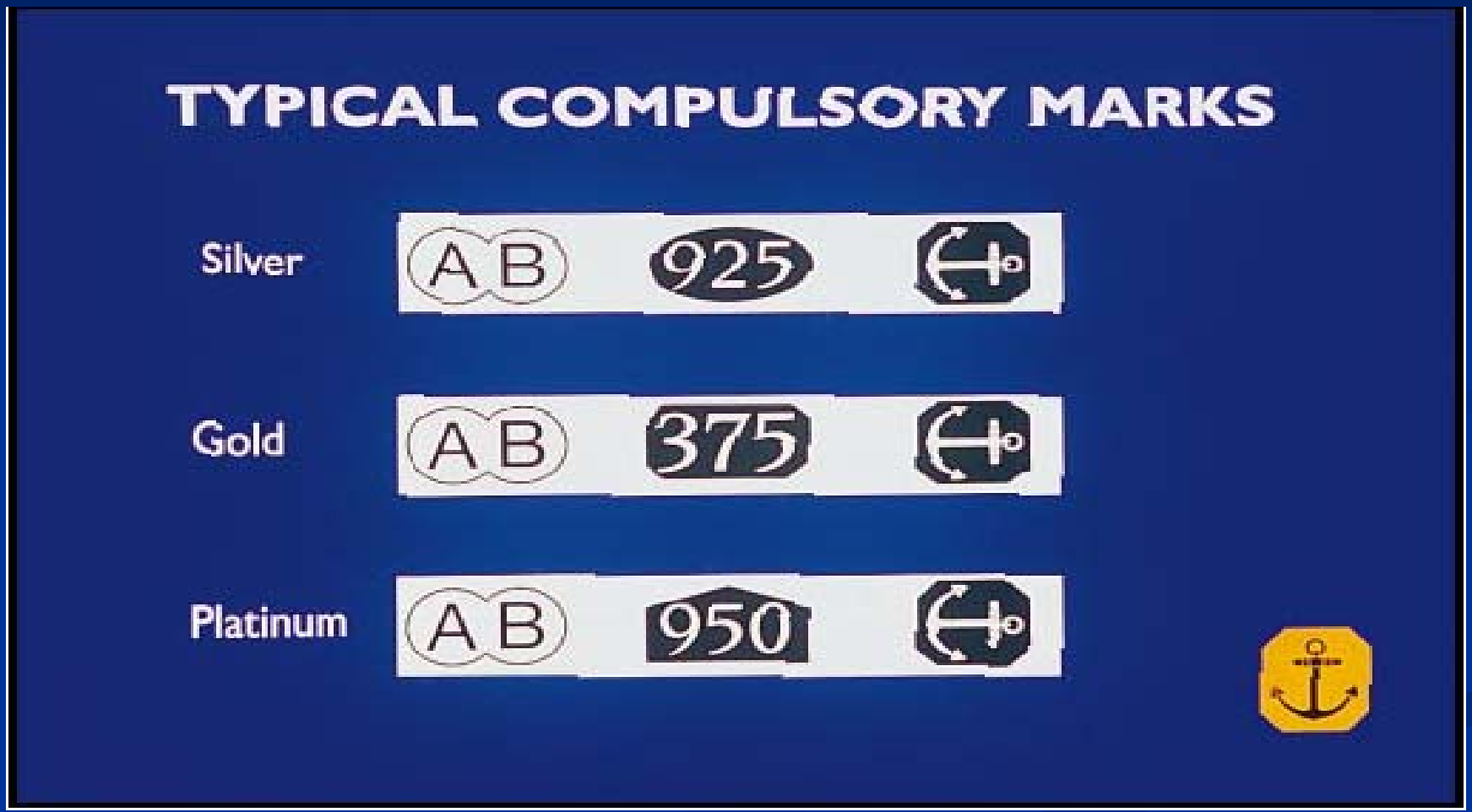
COUNTRIES CONSIDERING AN INDEPENDENT HALLMARKING SYSTEM

Abu Dhabi
Dubai
Saudi Arabia
South Africa

MAJOR JEWELLERY COUNTRIES WITHOUT AN INDEPENDENT HALLMARKING SYSTEM

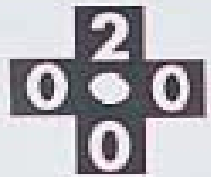
Canada
Germany
Italy
Japan
Taiwan
Thailand
United States

U.K. Hallmark System



U.K. Hallmark System

OPTIONAL MARKS

Symbol	Year	Convention	Millennium
			
All Standards	Date Letter (1999)	On Agreed Standards	Millennium mark 1999/20000 only

Fineness in the U.K.

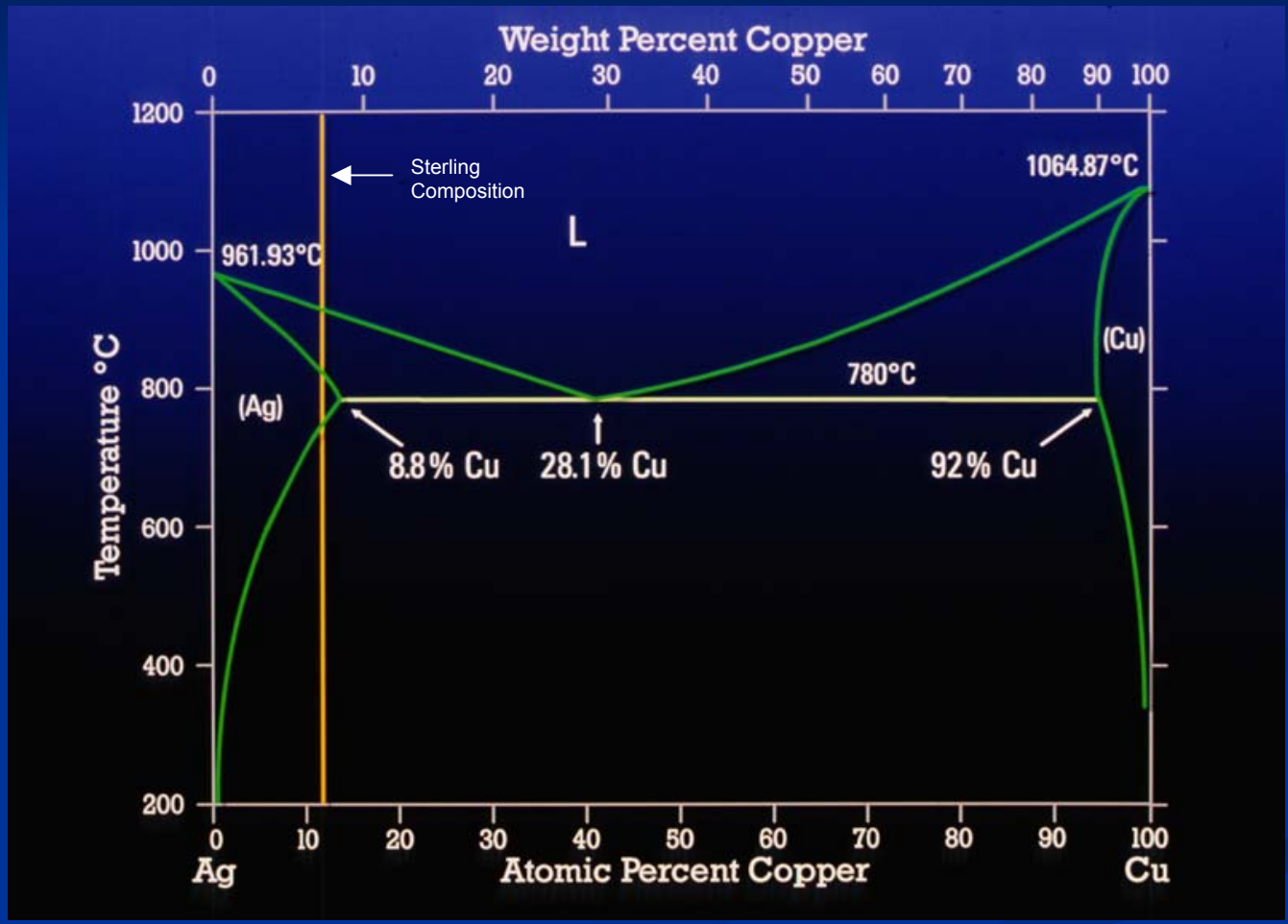
The standards of fineness allowable in the UK

GOLD	SILVER	PLATINUM
375	800	850
585	925	900
750	958	950
916	999	999
990		
999		

Sterling Silver

- 92.5% Ag minimum
- Balance: most commonly Copper
  - Solubility
  - Strength, Formability
  - Age Hardening
  - Recyclability
  - Color, Luster
  - Patina

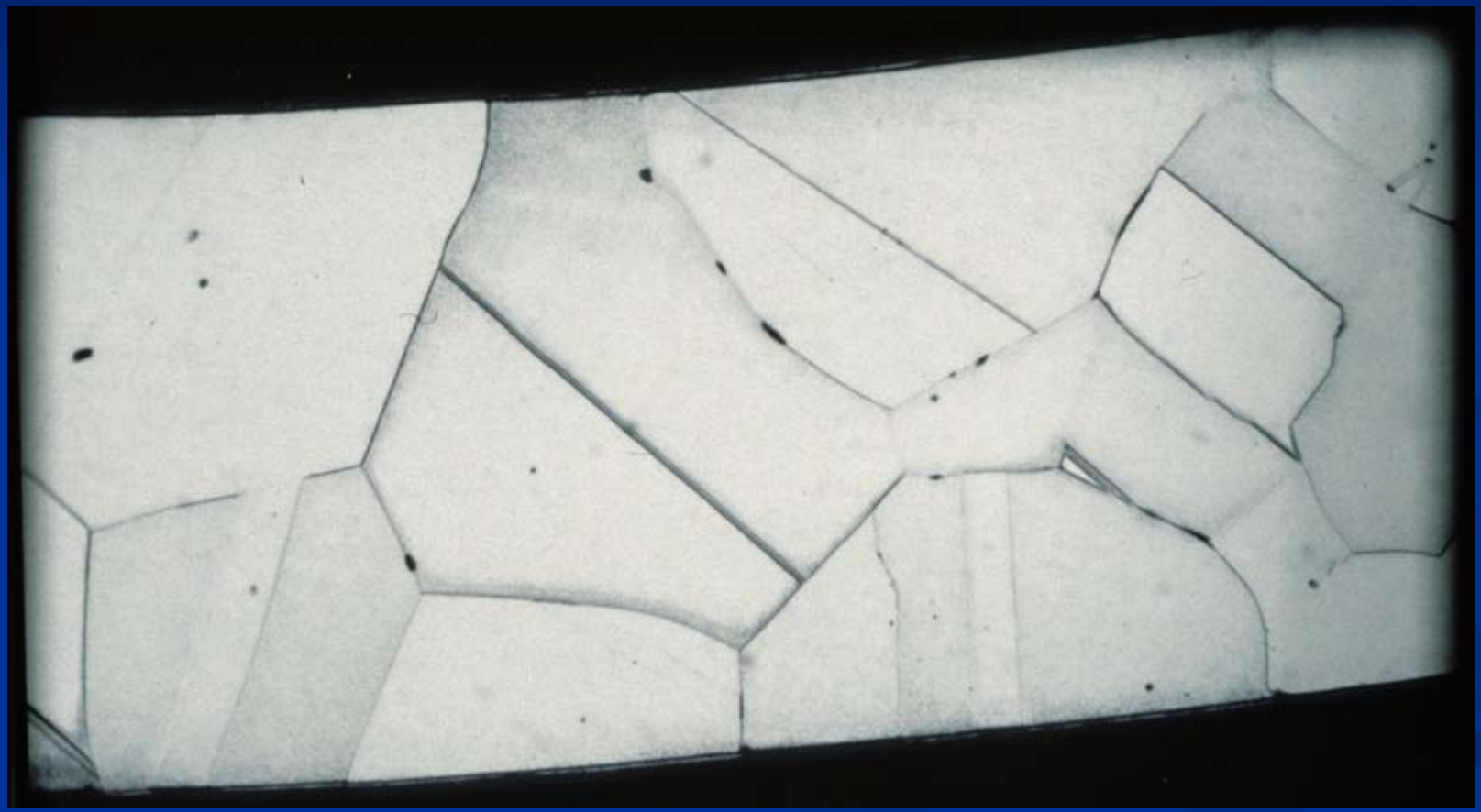
Silver-Copper Phase Diagram



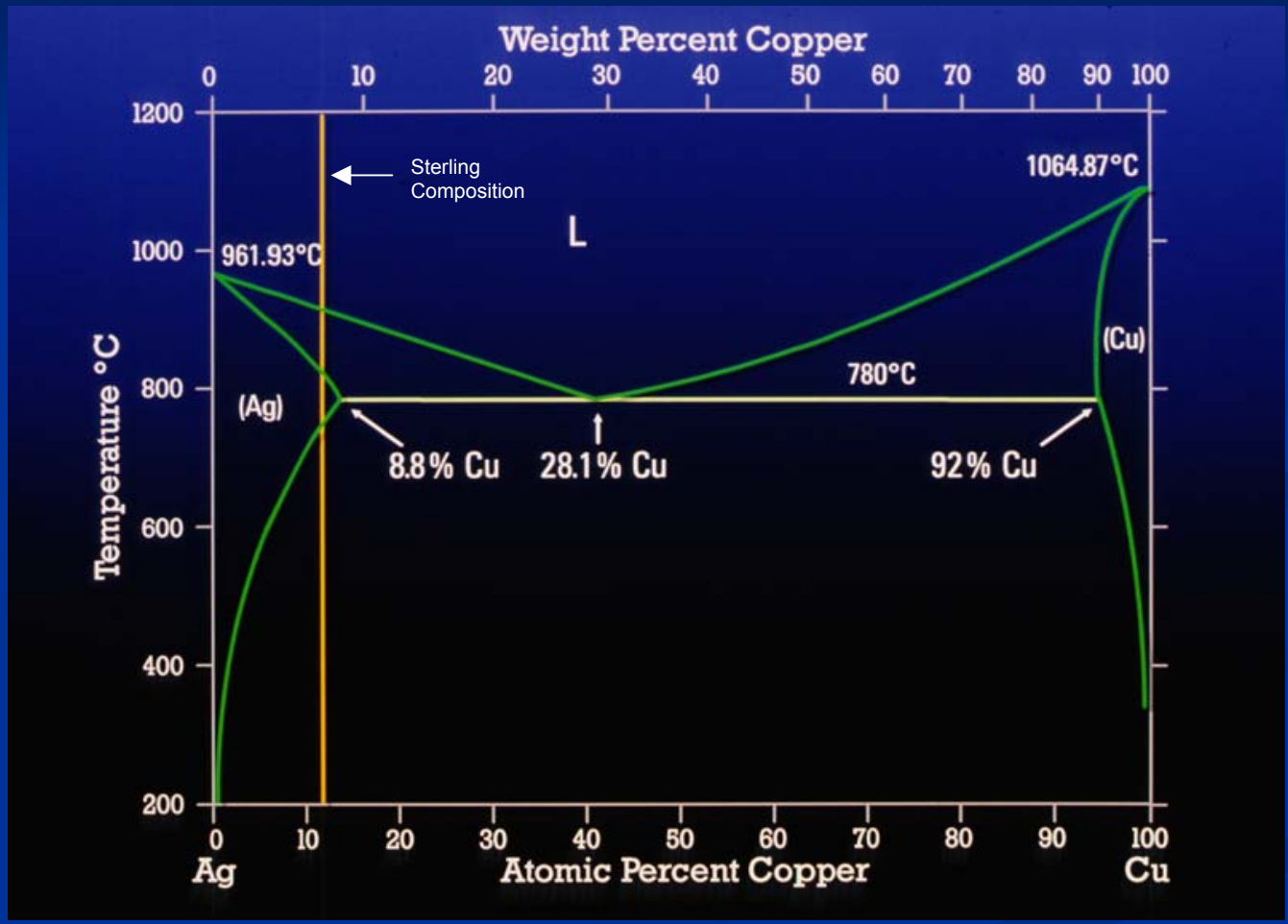
Microstructure of Investment Cast Sterling Silver Ring (x250)

Microstructure of Continuous Cast Sterling Silver Rod, 0.400” diameter (x250)

Microstructure of 0.010” thick Sterling Silver Strip, Solution Treated at 765C (x250)



Silver-Copper Phase Diagram



Microstructure of 0.010” thick Sterling Silver Strip, Solution Treated at 726C (x250)

Oxygen in Silver

Silver Oxide is unstable at T>455 C (851 F)

At One Atmosphere,
Solubility of O in Ag above m.p.= 0.3%
Solubility of O in Ag below m.p.= 0.006% (50 times less)

Thus, O is released during solidification!

"Spit", Porosity, Oxides of base metals

Deoxidation of Silver

Carbon Reduction:

$C + \underline{O} = CO$

Also, can use scavenger inert gas (Ar)

In silver / copper alloys:

$C + Cu_2O = 2Cu + CO$

$C + CuO = Cu + CO$

Deoxidation of Sterling Silver

- After carbon reduction, add phosphorus
- Good scavenger, forms P_2O_5 (slag)
- Small amount, ~ 0.02%
- Add as "master alloy": 85% Cu – 15% P

Reticulation

- Technique to apply “texture”
- Melt core of alloy, not the surface
- i.e. 80Ag-20Cu, heat / chemically treated
- Oxidize the copper, then pickle
- Surface rich in Ag, higher melting point
- Much like depletion gilding!

Reticulation of 80Ag-20Cu

Reticulation of 80Ag-20Cu

Reticulation of 14 Kt Gold

Reticulation in Jewelry

Reticulation in Jewelry

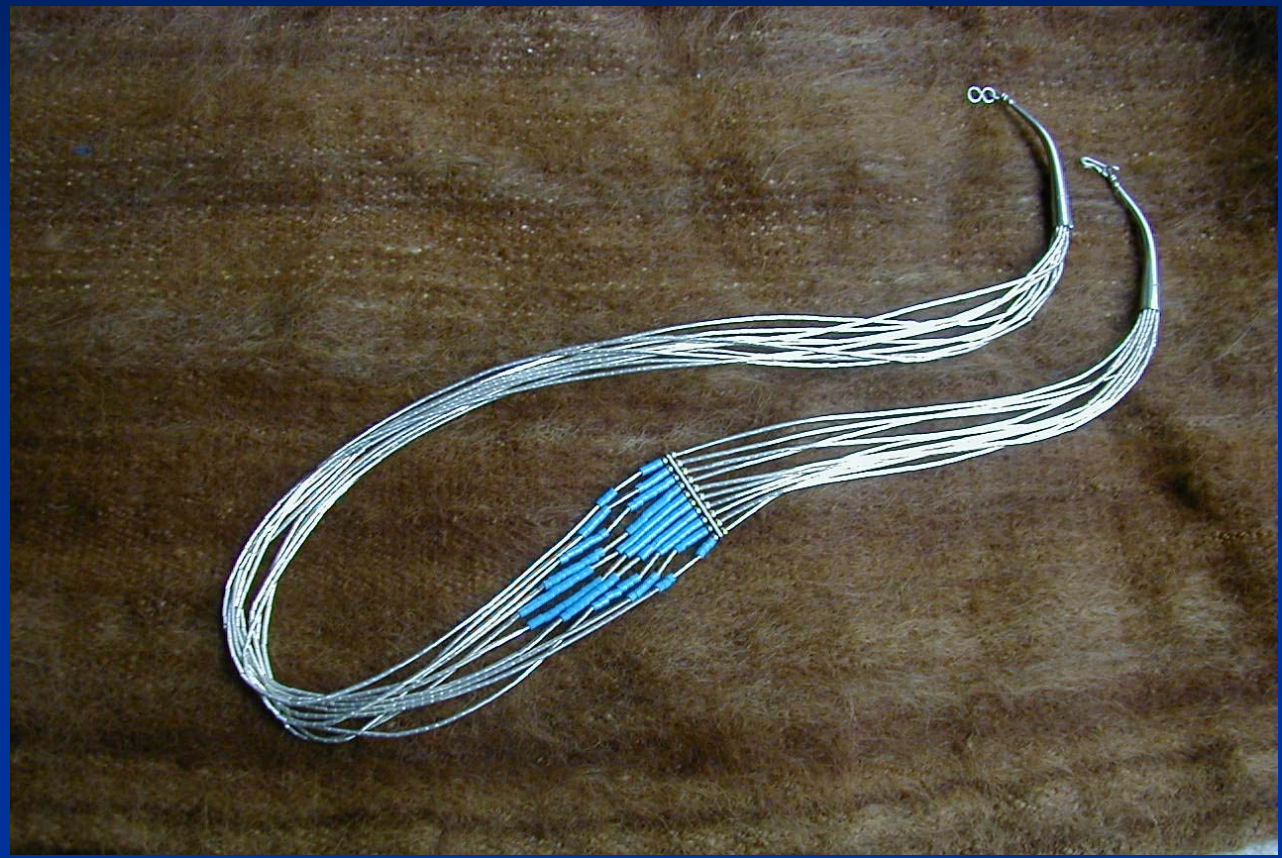
Fire Stain or Fire Scale

- Results from annealing or heat treating silver / copper alloys (oxidation of copper)
- Tenacious, can be removed by pickling
- Development of "alternative" Sterling Silver formulations, containing Zn, Sn, Ge
- Some claim "anti-tarnish"
- Mixed Success…..
- "Traditional" Ag/Cu works well!

Heishi

- American Indian Jewelry
- *Heishi*: Tiny beads from natural materials, hand made into precise sizes with a hole so they can be strung into necklaces
- Silver Heishi Beads, or *liquid silver* beads
- Made from silver strip

Heishi Necklace



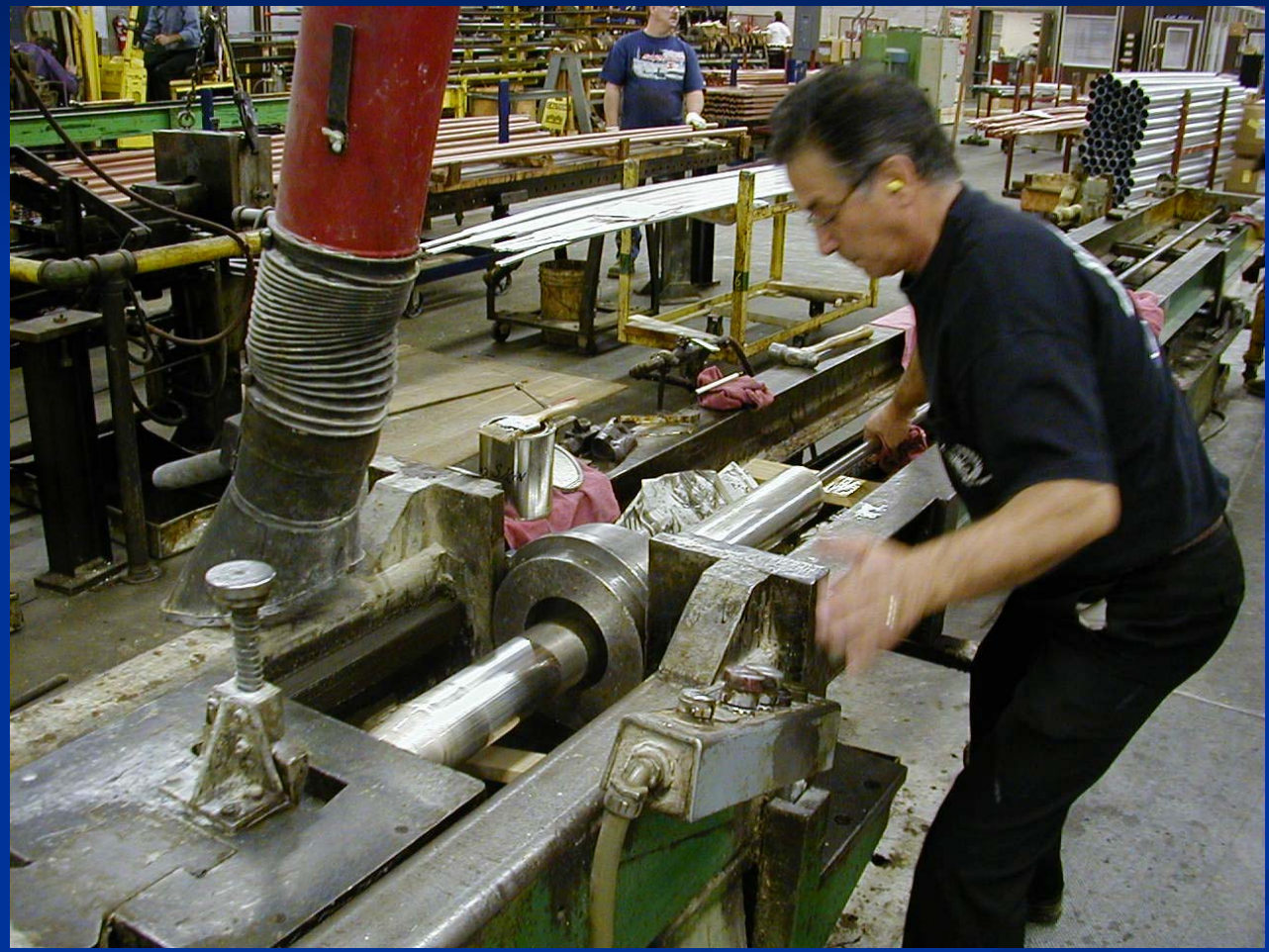
Contrasting Application:

Very Large Silver Tubes

Cast / Machined Silver Billet

Cast / Machined / Etched Silver Billets

Tube Drawing



Tube Drawing

Silver Tube, 3.5” diameter

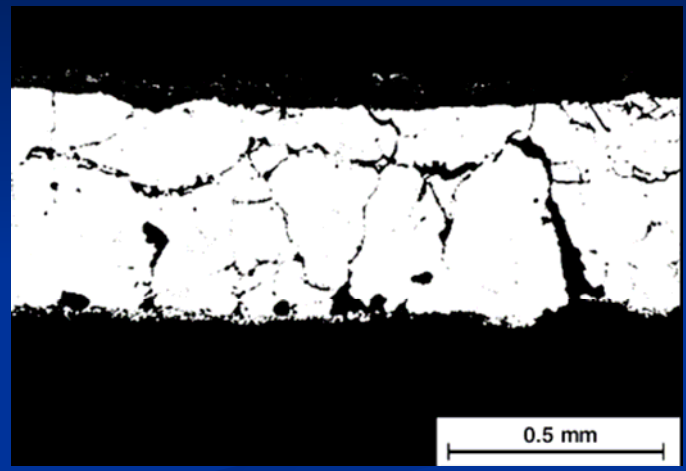
Silver Tubing

Embrittlement of Ancient Silver

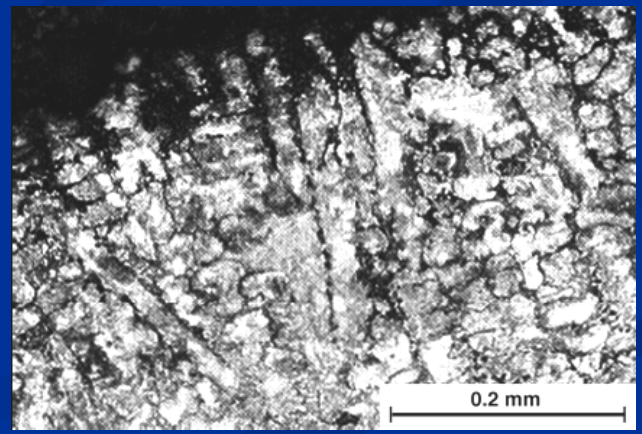
- R.J.H Wanhill, *Embrittlement of Ancient Silver*, Journal of Failure Analysis and Prevention, Volume 5 (1), February 2005
- Causes of Embrittlement:
  - Corrosion Induced
  - Microstructurally Induced
  - Synergistic effect
- Knowledge = Restoration and Conservation

Embrittlement of Ancient Silver (Cont.)

- *Intergranular Corrosion*, typical of mechanically worked / annealed objects

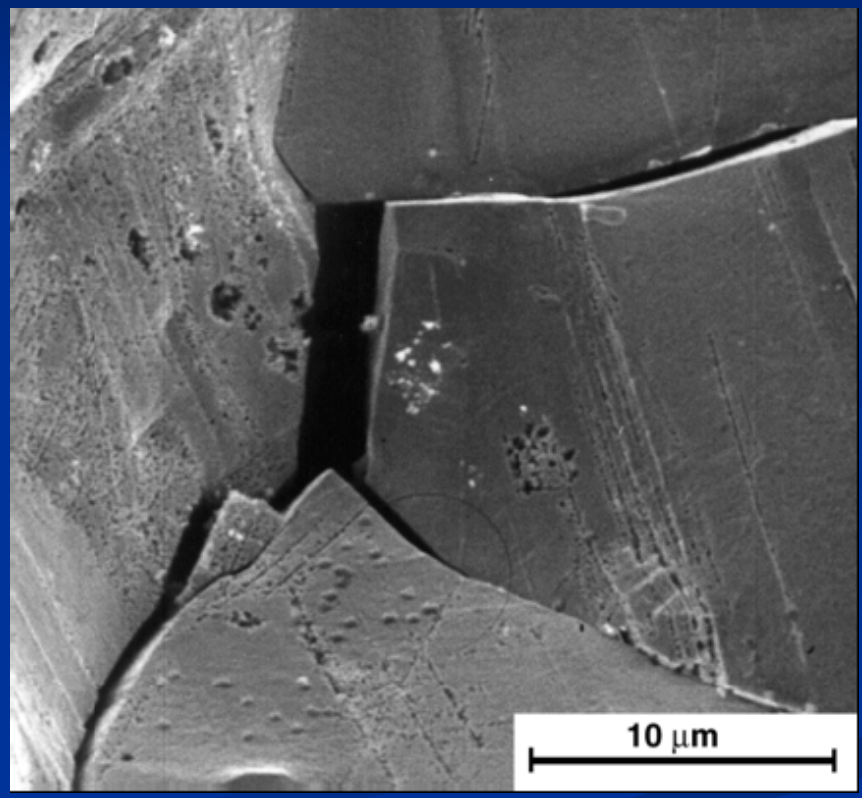


- *Interdendritic Corrosion*, due to copper segregation upon solidification



Embrittlement of Ancient Silver (Cont.)

- *Microstructurally Induced Embrittlement*, intergranular fracture due to impurity elements (Pb, Bi) segregating to grain boundaries



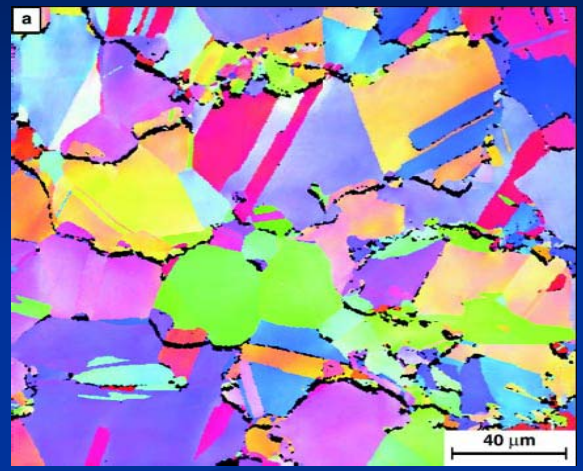
Embrittlement of Ancient Silver (Cont.)

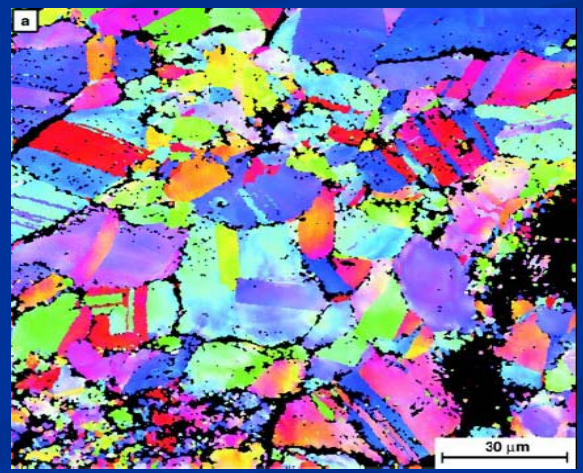
Gundestrup Cauldron

- 2nd or 1st century B.C.
- Metallography
- Field Emission SEM
- Electron Backscatter Diffraction

Embrittlement of Ancient Silver (Cont.)

- Annealed, free of corrosion
- Remanent cold deformation, corrosion damage
- *Conclusion*: cold deformation was primarily responsible for corrosion





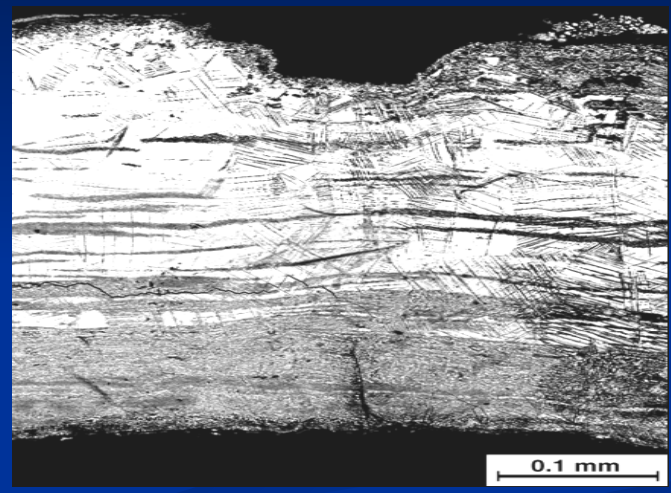
Embrittlement of Ancient Silver (Cont.)

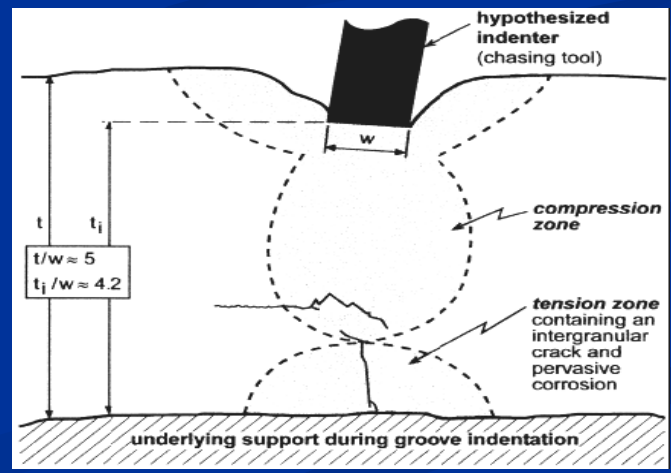
Egyptian Vase

- Ptolemaic Period, between 300 and 200 B.C.
- Metallography
- SEM
- EDX: 97.1%Ag, 0.9%Cu, 0.7%Pb, 0.3%Sb

Embrittlement of Ancient Silver (Cont.)

- Corrosion along slip lines (deformation)
- Link between remnant cold deformation and corrosion damage
- Microstructurally-induced embrittlement, 0.7%Pb
- Synergistic effect





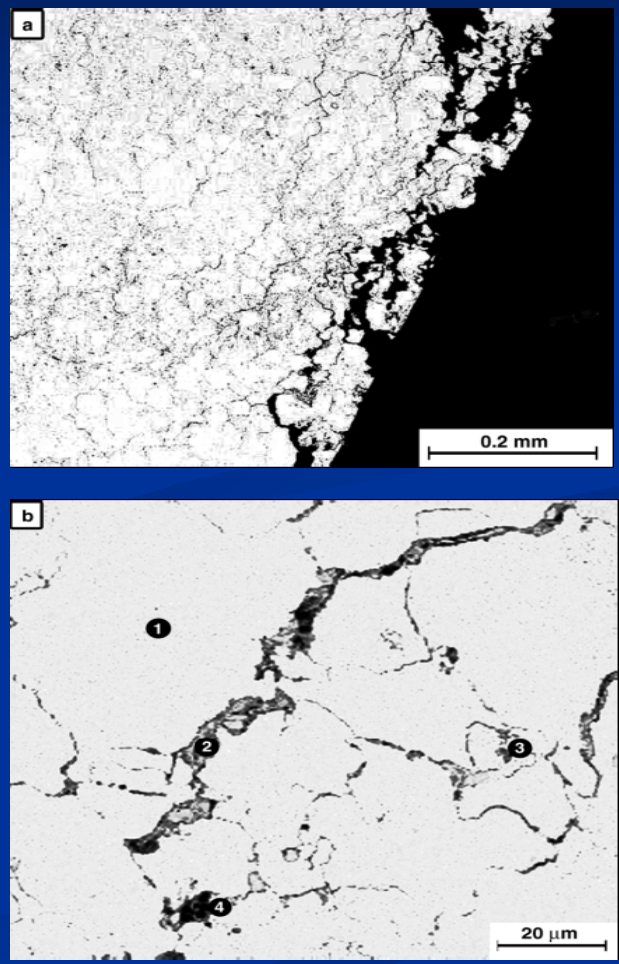
Embrittlement of Ancient Silver (Cont.)

Byzantine Paten

- Circa 600 A.D.
- Extensive breakage along annular decorating grooves

Embrittlement of Ancient Silver (Cont.)

- Intergranular corrosion at surface
- Copper precipitation at grain boundaries
- *Conclusion:* preferential corrosion along decorating grooves, thus most corrosion was due to remanent cold deformation



Embrittlement of Ancient Silver (Cont.)

Remedial Measures (reversible?)

- Corrosion Protection
  - Cleaning (*hydrogen plasma reduction*, reduces corrosion products to metallic silver)
  - Outgassing (dry the moisture)
  - Protective coatings (*Parylene-type* are very thin and uniform)
- Heat Treatment
  - Relatively high temperature
  - Risk of incipient melting
  - Problem with soldered joints, inlays, etc.
  - Irreversible

Platinum Group Metals (PGM)

- Platinum
- Palladium
- Iridium
- Ruthenium
- Rhodium
- Osmium

Platinum

- 950/1000 pure Pt: Platinum
- 950/1000 PGM, 750/1000 Pt:

  i.e. Ir-Pt
- 950/1000 PGM, 500/1000 Pt:

  i.e. 600Pt-300Ir-100Pd

Common Platinum Alloys

- Pt-5% Ru
- Pt-5% Ir
- Pt-5% Pd
- Pt-5% Co
- Pt-10% Ir

All are “harder” than pure platinum

Melting of Platinum

- Very high Melting Point: 3214 F (1768 C)
- Very reactive when molten. Keep Clean!
- Must be degassed
- Scrap accountability!

If you do everything right…….

Platinum Tubing

The End!

- Overview of Precious Metals
- Metallurgy
- Touched on some relevant topics
- Expand knowledge!
- My e-mail: aldoreti@alum.mit.edu

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