THE POWER OF METALS IN THE ANDEAN WORLD:
Laboratory Manual

INTRODUCTION:

This manual is divided into two components: laboratory protocols and metallographic examination of selected artifacts from Pre-Columbian Ecuador and Colombia.

The protocols take the investigator through the steps necessary for
1) smelting copper metal from copper oxide ore;
2) casting molten copper-silver alloy into a mold; and
3) working, annealing, and pickling the cast blank in order to achieve the final shape and produce a silver-enriched surface.

The case studies from Ecuador and Colombia illustrate metallurgical examination of samples removed from the artifacts by techniques that include sample preparation, polishing, etching, and interpretation of sample microstructures. These analytical techniques help the investigator to determine methods of manufacture.

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THE POWER OF METAL IN THE ANDEAN WORLD/ Laboratory

<u>**A Series of Copper-Silver Alloys**</u>

Please study the specimens and answer the questions posed for each. In describing the microstructures, make whatever drawings are necessary to clarify your descriptions. All observations (notes and drawings) should be recorded in your laboratory notebook.

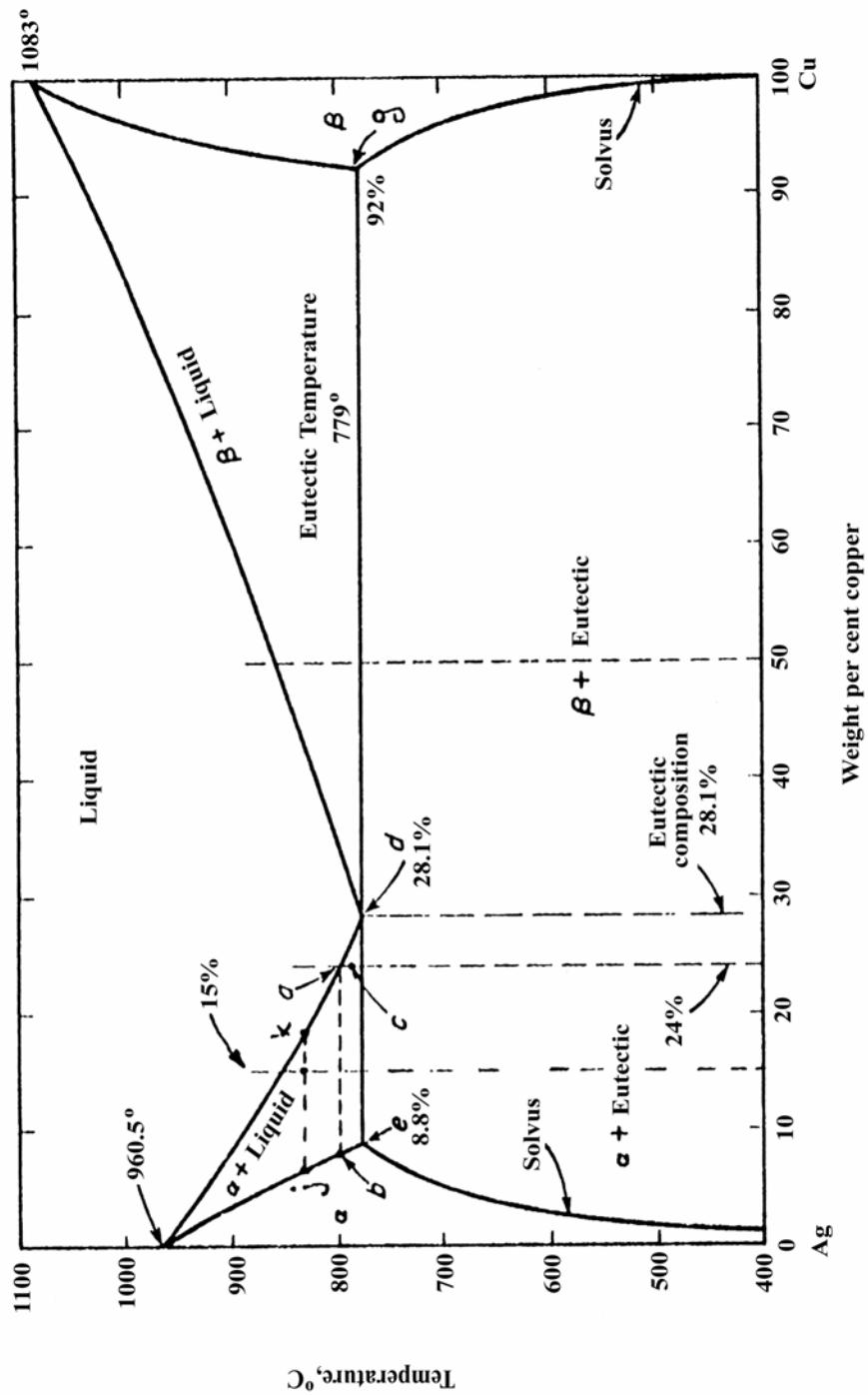<u>SPECIMEN A</u>: 25.5% Cu, 74.5% Ag

<u>SPECIMEN B</u>: 34.4% Cu, 65.5% Ag

<u>SPECIMEN C</u>: 60.4% Cu, 39.6% Ag

Which of these alloys is a hypoeutectic alloy? Which is a hypereutectic alloy? What phase is represented by the dendrites in Specimen A; what phase is represented by the dendrites in specimen B? Why are the dendrites in specimens A and B different colors (different shades of gray in the photomicrographs), since both samples were etched with the same etchant ($FeCl_3$)? What material surrounds the primary dendrites in all these samples (specimens A, B, C)?
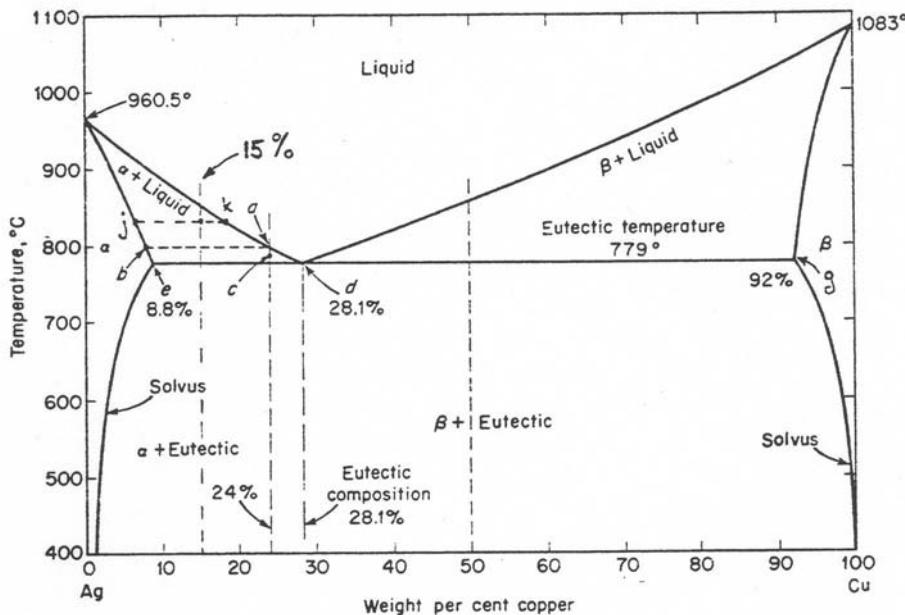
To assist you in answering these questions, refer to the Cu-Ag phase diagram and the information on the solidification in eutectic systems that follow.

Copper-Silver phase diagram

Copper-Silver phase diagram

SOLIDIFICATION IN EUTECTIC SYSTEMS

The copper-silver alloy system will be used as an example of solidification in eutectic systems.

1. Silver will hold up to 8.8% copper in solid solution. Thus any Ag-Cu alloy which lies within the composition range of 0 -8.8% Cu, when molten, will solidify with the formation of crystals of a solid solution. The composition of the α solid will be the same as that of the original liquid from which it forms (though the a grains may be cored). Thus α grains may range in composition from close to 100% Ag to 91.2% Ag/8.8% Cu, depending upon the composition of the liquid. Alpha grains are always single phase.

The same process takes place at the copper-rich side of the constitution diagram. Copper will hold up to 8% silver in solid solution. Any Ag-Cu alloy which lies within the composition range of 0-8% Ag, when molten, will solidify with the formation of β solid solution. These β grains will range in composition from almost 100% Cu to 92% Cu/8% Ag, depending upon the composition of the origina11iquid. The solid solution that forms has the same composition as the liquid from which it formed, and all β grains are single phase.

2. Silver can hold no more than 8.8% Cu in solid solution. It is essentially saturated with copper at that composition, and its matrix cannot accommodate more copper atoms. Similarly, copper is saturated with silver at the concentration level of 8% silver. No more silver atoms can be held by the copper matrix.

For alloys between the composition range of 91.2% Ag/8.8% Cu and 92% Cu/8% Ag another mechanism operates during solidification to handle the liquid that is beyond the limits of the two solid solution fields.

3. Consider an alloy of 15% Cu, 85% Ag. It will begin to freeze at about 850°C (where the vertical line representing that alloy intersects the liquidus curve). Small nuclei of α solid solution will form in the α + Liquid field (note that this is a 2-phase field). As the temperature of the alloy drops, these primary a crystals will grow as more liquid freezes. At any temperature, the compositions of the growing α grains and of the remaining liquid are given by the intersections of a horizontal tie line, drawn at that temperature, with the solidus and liquidus curves.

For example, at about 830°C, the composition of the primary α grains growing in the liquid is given by point j: 6% Cu in 94% Ag. The composition of the remaining liquid at this temperature is given by point k: 18% Cu in 82% Ag.

4. As the temperature continues to drop, the primary α grains continue to grow and less and less liquid remains. At 800°C the composition of the primary α grains is given by point b: 8% Cu, 92% Ag. The composition of the remaining liquid is given by point a: 25% Cu, 76% Ag.

5. When the temperature drops further and reaches 779°C, the primary α grains have reached the saturation concentration of copper in silver, given by point e: 8.8% Cu in 91.2% Ag. The remaining liquid has reached the composition of the eutectic alloy, given by point d: 28.1% Cu in 71.9% Ag. At this temperature the primary α crystals have grown as large as they can; no more a crystals can form. All of the remaining liquid freezes through the eutectic transformation. When the primary α crystals have grown dendritica11y, the eutectic solid or eutectic microconstituent will fill in the spaces between α dendrite arms to complete the solid grain.

6. Referring to the Ag-Cu constitution diagram, all alloys below 779°C will be solid. This temperature is known as the eutectic temperature and represents the lowest freezing point of any alloy in the entire system.

In the copper-silver system, all alloy compositions consisting of less than 28.1% copper, that is, below the eutectic composition, are known as hypoeutectic alloys. All alloy compositions with more than 28.1% copper, that is above the eutectic composition, are known as hypereutectic alloys.

In the phase diagram illustrated, all solid to the left of the eutectic composition will be composed of primary α phase surrounded by eutectic microconstituent; all solid to the right of the eutectic composition will be composed of primary β phase surrounded by eutectic microconstituent. Note, however, that the eutectic microconstituent is identical in composition no matter whether it has formed from eutectic alloy (alloy of eutectic composition), from liquid in the α + Liquid field or from liquid in the β + Liquid field. The eutectic microconstituent always forms from liquid that has arrived at the eutectic

composition, in this case 28.1% Cu 71.9% Ag. When it freezes it will always form the same eutectic solid.

7. The eutectic solid is a two-phase solid composed of a finely divided mixture of small grains of the α solid solution and the β solid solution. If one considers liquid that has reached the eutectic composition and is at the eutectic temperature, a tie line (known as the eutectic horizontal) drawn through this point will intersect the α and β solid solutions.

Thus the eutectic liquid freezes to form solid composed of α and β phases that are in intimate association.

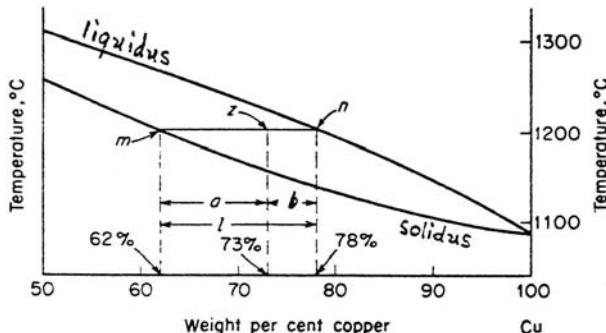| Phase	Composition
α solid solution	8.8% Cu, 91.2% Ag
eutectic liquid	28.1% Cu, 71.9% Ag
β solid solution	92% Cu, 8% Ag

Since the α solid solution needs more Ag than the liquid contains in order to form; since the β solid solution needs more Cu than the liquid contains in order to form, the two solid solutions form contiguously in the liquid, each solid giving up to the other the component it has to lose and obtaining from the other the component it has to gain. This sharing occurs by solid state diffusion of silver and copper atoms across the common boundary between adjacent solid phases.

8. Within that portion of the phase diagram where the eutectic transformation occurs, the primary α or primary β crystals never change their composition, i.e. they are always at the saturation composition of the α and β solid solutions. It does not matter what the composition of the original molten alloy is.

       The composition of the molten alloy determines:
       a) Whether primary α crystals will form or whether primary β crystals will form during solidification.
       b) The proportion of primary α (or primary β) and of eutectic microconstituent in the final solid (i.e. the ratio of α to eutectic or the volume fraction of one with respect to the other).

9. The lever law is a convenient way to predict the amount of any phase that will be present upon solidification of a given alloy. Consider the following diagram which represents part of an equilibrium phase diagram showing a liquid region, a solid region, and a 2-phase liquid + solid region.

The lever rule.

Given a point such as z which lies inside a two-phase region:
a) Find the composition of the two phases. Draw a tie line through z. The intersections of the tie line with the boundaries of the 2-phase region (points m and n) determine the composition of the phases.
b) Find the relative amounts of the two phases. Determine the three distances a, b, and 1 (in units of percent composition). The amount of the phase corresponding to point m (here, the solid) is given by the ratio b/l, while that corresponding to point n (here, the liquid) is given by a/l .

10. Let us apply the lever rule to three different alloys in the Ag-Cu diagram.

1) The 15% alloy (i.e. 15% Cu, 85% Ag)
Determine the relative amounts of primary alpha of the eutectic microconstituent when all the liquid has solidified.

m = 91.2% Ag	a = 91.2 -85 = 6.2
n = 71.9% Ag	b = 85 -71.9 = 13.1
z = 85% Ag	l = 91.2 -71.9 = 19.3

amount of α = 13.1/19.3 = 67.8%

the remaining portion of the solid must be eutectic: 100 -67.8 = 32.2% or amount of eutectic = 6.2/19.3 = 32.1%

2) The 24% alloy (i.e. 24% Cu, 76% Ag)
Determine the relative amounts of primary alpha and of the eutectic microconstituent when all the liquid has solidified.

m = 91.2% Ag	a = 91.2 -76 = 15.2
n = 71.9% Ag	b = 76 -71.9 = 4.1
z = 76% Ag	l = 91.2 -71.9 = 19.3

amount of α = 4.1/19.3 = 21.3%

N.B. The amount of α is considerably less than for the 15% alloy, as would be expected, since the α grains solidify through a small drop in temperature and do not have much chance to grow.
The remaining portion of the solid must be eutectic: 100 - 21.3 = 78.7%

3) The eutectic alloy (i.e. 28.1% Cu, 71.9% Ag)
This time, we are in a 2-phase field in which both phases are solid: the α phase and the β phase which, together, form the eutectic microconstituent. Determine the relative amounts of α and β in the eutectic:

For α: m = 91.2 (100-8.8)   a = 91.2-71.9 = 19.3
              n = 8.0   b = 71.9 – 8 = 63.9
              z = 71.9 (100-28.1)   l = 91.2 – 8 = 83.2

amount of α = 63.9/83.2 = 76.8%
The remainder must be β: 100 – 76.8 = 23.2%
Or β = 19.3/83.2 = 23.2%

The ratio of α to β in the eutectic microconstituent formed upon solidification of the 15% and the 24% alloys will be exactly the same as their ratio in example #3. There will be less eutectic formed in examples #1 and #2, but within the eutectic, the ratio of α to β is constant.