

# OPENING OF SECRET OF ETRUSCAN DECORATIONS FROM GOLD

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## Introduction

Etruscan gold jewelry beads (diameter 0,2 mm), which were soldered to the copper slabs, were found during excavations in the Apennine peninsula. For centuries, it was remained a mystery, how they have managed to combine gold with copper. Only in the 30-ies of the last century, scientists have determined that this was due to the formation between copper and gold an eutectic layer at a temperature less the temperature of fusion [1].

However, till now, it remained a secret of a composition of eutectics, or a way to obtain spherical beads of gold, nor the mechanism of formation of eutectics, because the atoms of both metals belong to the same group and, therefore, have the same  $d^{10}s^1$  - configuration of valence electrons.

## Results and discussion

We conducted experimental researches of obtaining spherical beads of copper powder in the filling of boron nitride [2]. A spherical beads with diameter of 0,1-0,2 mm were formed during heating a mixture in argon environment or in a vacuum to the temperature of fusion of copper. To increase the diameter of beads, we pressed in the mixture into the form of briquettes under the pressure of 200-500 MPa. This led to a convergence of multiple particles of copper into groups. Now, during the fusion of copper in briquettes, the size of beads increased to 1-2,5 mm (Table 1).

The effect of transforming a spontaneous form of particle in a spherical shape is achieved due to the inert-insulating component of boron nitride during the temperature of fusion of copper does not interact with it and do not wet by a copper, but firmly sticks to the drops of alloy, and when these drops are cooled an inert-insulating component of boron nitride exfoliate from them. The amount of a filling was chosen (8-12%) just to isolate the particles of copper between each other. The correlation of powder by size was  $K_3/K_M = 0,3$ , where  $K_3$  and  $K_M$  - are average size of initial powders of a filling (10-32 microns) and a copper (40-100 microns). The optimum system is Cu-8% BN: it provides a spherical copper particles of

diameter up to 2,5 mm at the lowest pressure of pressing about 300 MPa.

Table 1. A fusion of copper particles in the filling of boron nitride at 1423 K.

| A pressure of pressing, MPa | A fusion of particles |           |               | The results of experiments                             |
|-----------------------------|-----------------------|-----------|---------------|--|
|                             | Diameter, mm          | Weight, g | Quantity, pc. |  |
| 200                         | BN                    | 10        | -             | A content of particles a diameter up to 1 mm about 1%  |
|                             | < 0,1                 | 75        | -             |  |
|                             | 0,1-0,3               | 13        | -             |  |
|                             | 0,4-1,0               | 1         | 26            |  |
| 300                         | BN                    | 10        | -             | A content of particles a diameter 0,1-1,3 mm about 35% |
|                             | <0,1                  | 50        | -             |  |
|                             | 0,1-0,9               | 30        | -             |  |
|                             | 1,0-1,3               | 5         | -             |  |
|                             | 2,0-2,5               | 5         | 32            |  |

As a result, the Etruscans could make a mixture of gold particles in a filling, for example from a volcanic ash, and fuse gold in it, with above mentioned way. They could select the size of beads by dispelling a golden sand with the same size of particles.

The second mystery which deals with the composition and mechanism of formation of eutectics and the related phenomenon of creation of eutectics in the contact area between a copper and a gold, tried to solve A.S. Steinberg [1].

According to his point of view the interaction of gold and copper occurs at the point of deflection on a liquidus line (Fig. 1) at  $T = 1183$  K and the content of 78% gold. However, this assumption is not true, because at this point, the alloy is in liquid-phase state and it occurs some fusing of beads. In addition, the author's introduced diagram is not eutectic. In this alloy a deflection of liquidus line shown as a negative deviation of Vegard's law. It points to the appearance of a chemical connection between copper and gold in a solid fluid due to the overlapping of shells and appearance of valence connections [3], but is not associated with the formation of the eutectic alloy.

We have developed a new, better way. We used copper alloy Cu-1% BN as coupling phase porous

iron particles in the composite Fe-(Cu-1% BN). During partial dissolution of iron in the copper fusion in the process of heating of composite material has occurred an active interaction of atoms of an iron with components of boron compounds BN, followed by complete dissolution of its inclusions and the formation of layers of an eutectic alloy on the basis of copper and atoms of freed boron. It was enough just 0,25% BN in the composite material to provide this process[4].

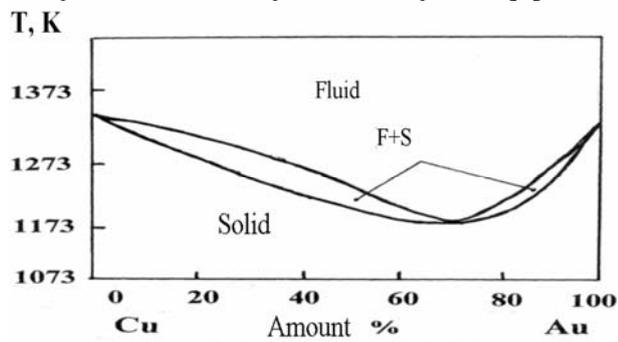


Fig.1. The state diagram for the alloy Cu-Au.

Thus, as a result of this research it was shows the mechanism of formation of eutectics, which takes place in the interaction of golden beads with a slab of copper, and it is discovered the cause of appearance of eutectics between them. It relates to the fact that the Etruscans used the natural gold, in which according to reference data contained from 5 to 30% of silver [5].

In the group of components of Cu, Ag, Au (Table 2) only copper with silver [6] form eutectics at  $T = 1063 \text{ K}$  (Fig. 2), and at a temperature of 120 K less than during formation of the liquid phase of Cu-Au in point of deflection on a liquidus line of alloy and at a temperature 273 K below the fusing temperature of gold, that ensured the Etruscans a high reliability of the connection of a copper plate with a golden beads. This technology of connection gold with copper deserves to be an example of a creative solution to the problem.

Table 2. Some properties of metals of copper subgroup [6].

| № | Elements | A name of a fluid                           |
|---|----------|---|
| 1 | Cu-Ag    | Form restricted solid fluids with eutectics |
| 2 | Cu-Au    | Form continuous solid fluids                |
| 3 | Ag-Au    | Form continuous solid fluids                |

There is an extensive opportunity to apply of spherical copper powders and iron-copper composite materials to create the type of chill casting moulds [7] and mould machines in today's production [8].

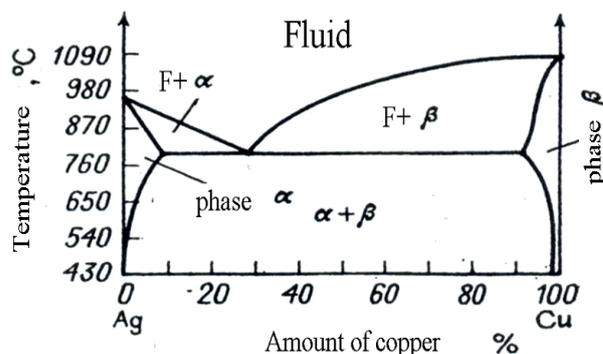


Fig.2. The state diagram for the alloy system Ag-Au.

## Conclusions

It was carried out an experimental research of the processes of obtaining spherical powders by melting into the filling out of boron nitride and composite materials of the iron-copper-boron nitride, on the basis of which the Etruscans discovered the technology of making gold jewelry that they brazed in a form of beads on a copper slab. The possibility of compound of gold to copper has been achieved due to creation layers of copper-silver eutectics between a copper slab and a gold bead in the process of heating gold to the temperature at 273 K lower temperature of fusion due to the presence of impurities of silver (5-30%) in natural gold. The resulted spherical powders and iron-copper composite materials are suitable for manufacturing of parts of casting moulds and mould machines.

## References

1. Штейнберг А.С. Репортаж из мира сплавов. – М.: Наука, 1989. – 556 с.
2. Черниенко В.В., Козлов В.Д., Александров И.П. и др. Способ укрупнения и сфероидизации порошков // Порошковая металлургия, 1989. – №5. – С. 12-15.
3. Григорович В.К. Электронное строение и термодинамика сплавов железа. – М: Наука, 1970. – 292 с.
4. Патент на винахід № 85110 МПК В 22 F 3\26. Спосіб одержання композиційного матеріалу на основі заліза \ Чернієнко В.В., Граменицький В.А., Шевцов СМ., Тігарєв В.М \ Оpubл. 25.12.2008. – Бюл. 24.
5. Гончаров А.М., Корнилов М.Ю. Справочник по химии. – К.: Высш. школа, 1977. – 304 с.
6. Кемпбел Дж. Современная общая химия. – Том 3. – М.: Мир, 1975. – 448 с.
7. А.с. СССР 1212693 МК В 22С 9\28. Сборный кокиль \Черниенко В.В.\ Оpubл. 23.02.1986. – Бюл. № 7.
8. А.с. СССР 1217568 МК В 22D. Кокильный станок для получения отливок типа тел вращения \ Черниенко В.В., Сухоруков Ю.Н., Машков А.К.\ Оpubл. 15.03.1986. – Бюл. №10.