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CERTAIN INTERESTING CRYSTALLINE ALLOYS.\*

BY RICHARD PEARCE.

In the treatment of auriferous copper containing bismuth, I have recently observed a small quantity of a grayish-white alloy, which on examination proved to be Bi containing in solution, as it were, a crystalline alloy of Bi and Au. This compound makes its appearance on the surface of the auriferous Cu in small globules as the latter cools.

These globules are rapidly attacked by nitric acid, and fine needle-shaped crystals of Bi and Au separate out. They are insoluble even in strong nitric acid.

On examination, the crystals were found to contain: Gold, 69.94 per cent.; silver, 0.63 per cent.; bismuth, 29.43 per cent. (No. 1).

The residue is very fusible, and at a temperature considerably below the melting-point it oxidizes rapidly, changing from its original gray color to greenish yellow (No. 2). On melting in a crucible under flux, a bronze-colored alloy is formed that has a specific gravity 15.47—somewhat higher than the calculated specific gravity of a simple mixture of the two metals in the proportion named.

In following out my investigations by repeated examinations of this alloy formed at different times, I found that, in dissolving a miscellaneous lot of alloy in nitric acid, some gold-yellow crystals were formed, which I succeeded in separating from the BiAu alloy by washing. These yellow crystals, under the microscope, showed distinct, regular, octahedral faces, and on examination they were found to be a crystalline alloy of Au and Ag in the proportion of 69 Au, 21 Ag (No. 3). The quantity was

\*Read also at New York meeting of the American Institute of Mining Engineers, February, 1885.

too small to admit of any very correct determinations of these crystals; but the peculiar feature was remarked that they contained Ag, while the BiAu crystals did not in any appreciable quantity.

My next experiment was to remelt some of the original Bi compound with Ag, so arranging that the Ag should exist in the melted alloy in the proportion of one atom of Au to one of Ag. The alloy was prepared by melting in a small crucible under a layer of borax, and then allowing the crucible, with its contents, to cool very slowly. This was done by placing the small crucible inside a larger crucible that had been previously made red-hot, and allowing the whole thing to stand until cold. The small crucible was then broken and the button of alloy detached. This alloy was found to be very brittle and crystalline. It was broken into lumps and treated in a flask with dilute nitric acid—one of acid to three of water. I found, after all the Bi had been attacked by the acid, that nothing was left behind but a beautiful crystalline alloy of Au and Ag (No. 4). There was an entire absence of any BiAu compound, which was found in former experiments. The solution of nitrate of Bi showed no trace of Ag. These crystals were found to contain: Gold, 62.164 per cent.; silver, 35.486 per cent.; Cu and Bi, 2.35 per cent. Further boiling of the crystals with strong nitric acid gave (No 5): Gold, 65.21; silver, 33.19; copper, 1.60.

Alloys of gold and silver in all proportions may be obtained in this way, depending on the amount of Ag used and also on the strength of nitric acid employed in the separation of the Bi. The largest and best formed crystals are, however, those in which the Au and Ag exist in the ratio of their atomic weights. Repeated boiling with strong nitric acid will, however, remove a portion of the Ag, without in any way damaging the crystals or effecting any very marked change in the color. In a number of experiments that I have made with alloys of Au and Ag, the lowest percentage of Au resulting from treatment with  $\text{HNO}_3$  was 58.51 (No. 6), and the highest 94.15 (No. 7).

#### ALLOYS OF GOLD AND COPPER.

Crystals of an alloy of Au and Cu may be obtained precisely

in the same way by substituting Cu for Ag. The form of crystals is the same, that of the regular octahedron, but they are much smaller. A crop of crystals was obtained having the composition 61.52 Au and 38.48 Cu (No. 8). On treating these crystals with strong nitric acid and boiling for some time until there was no further action, a large percentage of the Cu was dissolved out and a product was obtained a little darker in color, containing 93.49 Au and 6.51 Cu (No. 9).

Crystals were also obtained containing all three metals, in the proportion: Gold, 60.16; silver, 21.21; copper, 18.63 (No. 10)

These experiments indicate that Au will not combine with Bi if Ag or Cu are present in sufficient quantity. The crystals of Au and Bi are in fine needle-shaped forms, the system of crystallization not determined; but possibly rhombohedral (the crystalline form of Bi).

Au, Ag and Cu crystallize out together from a solution of these metals in Bi; the mother liquor, if I may use the expression, containing no Ag or Cu unless these metals are present in excess of what is required to form alloys that will resist the action of dilute nitric acid.

The following experiment was made with a view to determining the solvent action of Bi, melted at a low temperature, on the crystals of alloy of Au and Ag formed by the process that I have described:

An alloy was made by melting Au and Ag in about their atomic proportions with Bi, and allowing to cool slowly. The alloy was then heated in a small iron ladle until it became liquid, care being taken not to increase the temperature much above the melting-point. The liquid portion was then poured off and the residue of crystals drained until a pasty mass was obtained. The temperature was then slightly increased, and a further quantity of molten Bi poured off. The percentage of each product was as follows: 56 per cent. of the total weight was poured off at the first melting at a low temperature; 19 per cent. after a slightly increased temperature; the rest, 25 per cent. (the pasty mass), re-treated with dilute nitric acid, gave a crop of good crystals, which were found to contain: Gold, 59.06; silver,

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37.21 (No. 11); Cu and Bi (by diff.), 3.73. Treated with strong nitric acid, their composition became: Gold, 68.53; silver, 27.54; copper, 3.93. I found in this experiment that the pasty residue in the ladle contained only about 62 per cent. of the total gold, the remainder being carried off by the liquated Bi.

The ratios of the gold and silver in these three products were as follows :

			(Approximately.)
First liquation . . . . .	Au 74.16	Ag 25.84	Au <sub>3</sub> Ag <sub>2</sub>
Second liquation . . . . .	Au 65.35	Ag 34.65	AuAg
Pasty residue . . . . .	Au 71.33	Ag 28.67	Au <sub>4</sub> Ag <sub>3</sub>

In all these alloys of Au, Ag and Cu, the only crystalline form observed was that of the regular octahedron without any modification.\*

ALLOYS OF BISMUTH AND PLATINUM.

Experiments were made to see how far it was possible to prepare in a similar way crystalline alloys of platinum and bismuth.

Pt and Bi were melted together and allowed to cool slowly in the usual way. The brittle alloy was treated first with dilute nitric acid and then with strong acid. A black crystalline powder was obtained, which, under the microscope, showed some few crystals, form not determined.

A second experiment was made with the addition of Cu to a similar mixture as before. A highly crystalline, jet-black residue was obtained, which, on examination, proved to be binoxide of platinum.

Crystalline alloys are obtained in the same way as with Au; but these compounds, unlike those containing Au, are decomposed by nitric acid; the metals Bi and Cu that entered into the composition of the alloy being entirely replaced by oxygen, and this without destroying the structure of the crystal, as will be seen by examination (No. 12). The black crystals became red-hot in a current of hydrogen, water being condensed on the sides of the tube, a grayish-white powder of Pt being left behind (No. 13). A loss of weight was sustained in this experi-

\*The Bi used for most of these alloys was somewhat impure, containing notably a little copper.

ment equal to 13.75 per cent., which is very near the amount of oxygen required by the formula of  $\text{PtO}_2$ . On heating in a tube, it gives off O, a grayish-white powder of Pt remaining.

The black crystals can be ground easily in a mortar without showing the slightest evidence of metallic particles. Alcohol is readily oxidized by this compound. On heating the crystals, a trace of reddish-brown gas is given off, probably due to a small quantity of occluded nitric oxide.

If it were possible to attack the Bi by some acid that is not oxidizing, we should unquestionably obtain crystals of the alloy of Pt and Bi, or Pt and Cu, or perhaps Pt, Bi, and Cu; but on using nitric acid as the solvent, we have to be content with pseudomorphs of  $\text{PtO}_2$ , after the alloy.

In order to avoid the use of nitric acid, an experiment was made by substituting Zn for Bi, in the hope that crystals would be formed that could be separated by dissolving out the Zn with  $\text{H}_2\text{SO}_4$ . A black powder was obtained in this way, showing, however, no evidence of crystallization. On treating the black powder with nitric acid, Cu is dissolved to the extent of 20 per cent., and a grayish-black residue was obtained, which, when dried, possessed highly oxidizing properties (No. 14). It instantly ignited a drop of alcohol and exploded a mixture of hydrogen and air. What the exact nature of this substance is, I have not determined; but it differs materially from the crystalline black substance prepared from the Bi alloy. From the loss sustained on ignition (less than one-half required for  $\text{PtO}_2$ ), it would appear to be finely divided platinum intimately mixed with  $\text{PtO}_2$ . Its oxidizing properties are, however, far more energetic than were shown by the previous compound.

These experiments that I have drawn attention to may be regarded as being of a preliminary character. They offer, however, a field for further investigation that would, in all probability, lead to some interesting facts connected with the composition of alloys.

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Specimens of tetradymite from Montana were presented to the Society by Mr. R. Pearce.