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THE PRODUCTION OF ALLOYS OF TUNGSTEN AND OF MOLYBDENUM IN THE ELECTRIC FURNACE.[1]

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INTRODUCTION.

WITH the introduction of the electric furnace, the new field of chemistry at high temperatures was opened to investigation. Moissan especially succeeded in reducing the most refractory oxides, and in volatilizing many of them, as well as certain metals which were considered infusible. He described[2] a method of preparing alloys of vanadium, using the pentoxide as the source of vanadium.

Bernoulli[3] prepared alloys of tungsten with copper, lead, bismuth, cobalt, nickel, etc. His method of working consisted in mixing the oxides of the two metals with lampblack, placing the mixture in a crucible and then heating it in an ordinary furnace. Proceeding in this manner he was not able to obtain alloys containing more than 10 per cent. of tungsten.

[1] From author's thesis presented for the degree of Doctor of Philosophy, University of Pennsylvania, 1900.

[2] "La Four Electrique," p. 246.

[3] Pogg. *Ann.*, III, 573.

Knowing the comparative ease with which tungsten and molybdenum are reduced from their oxides, it was thought that it might be possible to mix these oxides with oxides of other metals and then reduce the mixture in the electric furnace, obtaining as a final product an alloy of the two metals.

In the following experiments the furnace used was of the type known as the "Moissan." The carbon for the reduction was prepared by ignition of cane-sugar. The crucibles were made of graphite, modeled in the form of an assay scorifier. This shape is preferable, as it allows the arc to play directly on the bottom of the crucible. In some of the experiments the crucibles were lined with magnesia, thus preventing the hot metal from absorbing any of the graphite.

Unless otherwise mentioned the graphite crucibles were used. After each reduction the furnace was closed and allowed to cool before removing the crucible containing the fusion.

Ten preliminary experiments were made with tungstic acid, attention being paid more particularly to the influence of the carbon, and to the variation in voltage and amperage. The results showed that the amount of carbon used exerted a greater influence in the purity of the metal than variations in the strength of current, and the duration of its action. The product invariably contained carbon and traces of unreduced oxide. An effort was made to burn out the carbon by heating the impure metal in magnesia-lined crucibles, but the metal was changed to trioxide and magnesium was volatilized.

ALLOYS OF TUNGSTEN.

Tungsten trioxide and bismuthic oxide were mixed in varying amounts with carbon and exposed for several minutes to the action of a current of 60 to 80 volts, and 75 to 150 amperes. The quantity of bismuth detected in the metallic product in no case exceeded 0.64 per cent.

When cupric oxide was substituted for the bismuthic oxide, and a current of 75 to 150 amperes and 60 to 80 volts was applied for five minutes a regulus remained which showed, upon analysis, 18.24 per cent. of tungsten, 77.73 per cent. of copper, and 3.23 per cent. of carbon. On using a crucible lined with magnesia the copper was completely expelled and tungsten trioxide remained.

The results obtained in attempting to prepare an alloy of tungsten and manganese were negative. Two trials were made with chromium with the following conditions:

Experiment I.—

2 grams of tungsten trioxide	Voltage, 72–80.
2 " " chromic oxide	Amperage, 100–160.
2 " " carbon	Time, 5 minutes.

The reduction was made in a lime crucible. The resulting globule of metal was very hard and brittle, its surface being covered with a layer of chromic oxide. Its interior was gray in color. The specific gravity of the alloy equaled 8.96. It showed, upon analysis, 2.87 per cent. of chromium and 97.64 per cent. of tungsten.

Experiment II.—

2 grams of tungsten trioxide	Voltage, 72–85.
2 " " carbon	Amperage, 100–150.
1 gram of chromic oxide	Time, 5 minutes.

A carbon crucible was used in this experiment, but alloys containing a higher percentage of chromium than given in Experiment I, were not prepared. The next trial was made upon tungsten trioxide and cobaltic oxide with these conditions:

2 grams of tungsten trioxide	Voltage, 70–80.
2 " " cobaltic oxide	Amperage, 125–150.
1 gram of carbon	Time, 1 minute.

The crucible was of lime and the button, which was strongly magnetic, very tough and tenacious, had the specific gravity 10.96. Its analysis showed 51.86 per cent. of tungsten, and 48.26 per cent. of cobalt.

Upon varying the conditions to

1 gram of tungsten trioxide	Voltage, 65–70,
3 grams of cobaltic oxide	Amperage, 110–130,
2 grams of carbon	Time, 2 minutes,

and using, as before, a lime crucible the resulting metallic globule was discovered to be strongly magnetic, very tough, and it was broken with difficulty. Its specific gravity was found to be 8.92. Its analysis revealed the presence of 29.24 per cent. of tungsten, and 70.10 per cent. of cobalt.

The experiments conducted with the oxides of tungsten and nickel gave very favorable results:

Experiment I.

2 grams of tungsten trioxide	Voltage, 68–80.
2 " " nickel oxide	Amperage, 100–135.
2 " " carbon	Time, 2 minutes.

The reduction was made in a crucible lined with magnesia, and a globule was obtained which was slightly magnetic, could be filed, and was very tough. Its specific gravity equaled 10.66. Its analysis gave 50.22 per cent. of tungsten, and 49.88 per cent. of nickel.

Experiment II.—

3 grams of tungsten trioxide	Voltage, 75–90.
2 " " carbon	Amperage, 100–175.
1 gram of nickel oxide	Time, 1½ minutes.

The crucible was similar to that used in Experiment I. The resulting button was very hard and non-magnetic, extremely brittle, and easily pulverized. Its specific gravity equaled 12.66. The analysis showed 91.19 per cent. of tungsten, and 8.08 per cent. of nickel.

Repeated attempts were made to alloy tin and tungsten after the plan pursued with the other metals, but without success. It would, therefore, appear that starting with the oxides it is possible to prepare alloys of tungsten with those metals which require a high temperature for their volatilization. In the case of those requiring a low temperature, the oxide is apparently reduced and the metal driven off before the tungstic oxide is reduced. Doubtless alloys of tungsten and the lower fusing metals could be prepared by starting with the metals and melting them together; but if this is attempted in the electric furnace the intense heat drives off the lower-fusing metal, leaving the one with a higher fusing-point in the furnace.

ALLOYS OF MOLYBDENUM.

Three reductions of bismuthic oxide and tungsten trioxide were made:

Experiment I.—

4 grams of molybdenum trioxide	Voltage, 65–70.
4 " " bismuth oxide	Amperage, 90–120.
1 gram of carbon	Time, 2 minutes.

The resulting metal was very hard. Its specific gravity equaled 6.81. It gave, upon analysis, 91.61 per cent. of molybdenum, 6.50 per cent. of bismuth, and 2.28 per cent. of carbon.

Experiment II.—

2 grams of molybdenum trioxide	Voltage, 60–70.
8 " " bismuth oxide	Amperage, 75–110.
1.5 " " carbon	Time, 2 minutes.

A granular mass was obtained after heating for one and one-half minutes. It was re-fused for one minute in a crucible lined with magnesia, and was converted into a very hard metallic button, having a specific gravity of 8.91. It showed, upon analysis, 92 per cent. of molybdenum, 4.81 per cent. of bismuth, and 3.90 per cent. of carbon.

Experiment III.—

6 grams of molybdenum trioxide	Voltage, 70–80.
2 " " bismuth oxide	Amperage, 100–150.
1 gram of carbon	Time, 2 minutes.

A crucible with magnesia lining was used in this experiment. The analysis showed 97.91 per cent. of molybdenum, 1.10 per cent. of bismuth, and 1.21 per cent. of carbon. All efforts looking to the formation of a molybdenum-copper alloy were fruitless.

In the case of molybdenum and manganese the results were good and entirely unlike those observed with tungsten and manganese, as will be noticed in the following experiments:

Experiment I.—

4 grams of molybdenum trioxide	Voltage, 75–85.
4 " " manganese dioxide	Amperage, 100–150.
3 " " carbon	Time, 2 minutes.

A button, having a specific gravity of 7.08, was obtained. It gave, upon analysis, 71.07 per cent. of molybdenum, 14.36 per cent. of manganese, 9.60 per cent. of iron, and 4.34 per cent. of carbon. The iron in this alloy came from the manganese dioxide.

Experiment II.—

2 grams of molybdenum trioxide	Voltage, 70–80.
6 " " manganese dioxide	Amperage, 100–130.
3 " " carbon	Time, 2 minutes.

The resulting alloy had the specific gravity 6.9. Its analysis

revealed the presence of 60.08 per cent. of molybdenum, 21.11 per cent. of manganese, 16.64 per cent. of iron, and 2.99 per cent. of carbon. My experience with molybdenum and chromium is briefly summarized in the following experiments:

Experiment I.—

2 grams of molybdenum trioxide	Voltage, 70–90.
6 " " chromic oxide	Amperage, 100–150.
2 " " carbon	Time, 3 minutes.

A carbon crucible was used in the reduction. Molybdenum trioxide, unmixed with carbon, was placed in the bottom of the crucible, and upon this trioxide was introduced a mixture of chromic oxide, the balance of the oxide of molybdenum and carbon. The product of the fusion was hard and brittle. Its specific gravity was found to be 6.53. Its analysis showed the presence of 12.82 per cent. of molybdenum, 76.71 per cent. of chromium, 7.52 per cent. of iron, and 2.55 per cent. of carbon.

Experiment II.—

4 grams of molybdenum trioxide	Voltage, 70–80.
4 " " chromic oxide	Amperage, 90–130.
3 " " carbon	Time, 3 minutes.

The alloy, steel-gray in color, proved to be hard and brittle. Its specific gravity was found to be 7.65, and upon analysis it showed 39.96 per cent. of molybdenum, 53.24 per cent. of chromium, and 6.22 per cent. of iron with a trace of carbon. An alloy of tin and molybdenum was not obtained.

Several trials were made with molybdenum and nickel oxides, but only those will be introduced here which gave definite results:

Experiment I.—

2 grams of molybdenum trioxide	Voltage, 70–80.
4 " " nickel oxide	Amperage, 75–125.
2 " " carbon	Time, 2 minutes.

The crucible was lined with magnesia for this fusion. The metal obtained was very hard and brittle, non-magnetic, and had a specific gravity of 7.61. Upon analysis it gave 17.72 per cent. of molybdenum, 80.93 per cent. of nickel, and 1.63 per cent. of carbon.

Experiment II.—

4 grams of molybdenum trioxide	Voltage, 75–80.
2 " " nickel oxide	Amperage, 100–150.
2 " " carbon	Time, 1 minute.

The alloy was soft and easily filed. It was non-magnetic and its specific gravity was found to be 8.00. Its analysis showed 65.10 per cent. of molybdenum, and 34.72 per cent. of nickel.

Experiment III.—

4 grams of molybdenum trioxide	Voltage, 73–75.
2 " " nickel oxide	Amperage, 140–160.
2 " " carbon	Time, 1 minute.

A graphite crucible was used in the reduction. The alloy was hard, brittle, and non-magnetic. Its specific gravity equaled 8.88. Its analysis showed the presence of 50.20 per cent. of nickel, 42.48 per cent. of molybdenum, 3.05 per cent. of carbon, and 4.04 per cent. of silica. The silica probably came from the material used in the manufacture of the graphite crucible.

The reduction of mixed oxides of molybdenum and cobalt was not attended with the least difficulty; indeed, from the appended results it would seem that these particular metals alloy in almost any proportion:

Experiment I.—

2 grams of molybdenum trioxide	Voltage, 68–75.
4 " " cobaltic oxide	Amperage, 100–175.
2 " " carbon	Time, 1½ minutes.

The crucible had a magnesia lining. The alloy was very hard, tough, and magnetic. Its specific gravity equaled 7.32. Its analysis gave 17.06 per cent. of molybdenum, and 82.34 per cent. of cobalt.

Experiment II.—

3 grams of molybdenum trioxide	Voltage, 70–90.
3 " " cobaltic oxide	Amperage, 100–160.
2 " " carbon	Time, 1½ minutes.

The crucible was lined with magnesia. The alloy was very hard, tough, and magnetic. Its specific gravity equaled 6.44. Its analysis showed 35.64 per cent. of molybdenum, 62.91 per cent. of cobalt, and 1.79 per cent. of carbon.

Experiment III.—

3 grams of molybdenum trioxide	Voltage, 75–80.
3 " " cobaltic oxide	Amperage, 175–190.
2 " " carbon	Time, 1½ minutes.

In this experiment I used a graphite crucible, and obtained an alloy that was hard, slightly magnetic, very brittle, and easily pulverized. The specific gravity was 6.94. Its analysis gave 47.10 per cent. of molybdenum, and 52.30 per cent. of cobalt.

Experiment IV.—

4 grams of molybdenum trioxide	Voltage, 75–95.
2 " " cobaltic oxide	Amperage, 125–175.
2 " " carbon	Time, 1½ minutes.

The crucible was lined with magnesia. The alloy was very hard, brittle, and feebly magnetic, with a specific gravity of 7.14. Its analysis gave 54.57 per cent. of molybdenum, and 45.35 per cent. of cobalt.

Experiment V.—

4 grams of molybdenum trioxide	Voltage, 70–100.
2 " " cobaltic oxide	Amperage, 110–150.
2 " " carbon	Time, 1½ minutes.

Here I used a graphite crucible, placing the molybdic oxide in the bottom. The alloy was soft enough to be filed, but was brittle and slightly magnetic. The specific gravity was 6.55. It gave, upon analysis, 49.47 per cent. of molybdenum, and 50.86 per cent. of cobalt.

While tungsten and molybdenum ordinarily show many similarities in their reactions, we observe in the preceding experiments differences not wholly devoid of interest. Thus, while tungsten and bismuth did not yield an alloy, with molybdenum and bismuth definite products did result. The experiments with tungsten and copper were positive, but with molybdenum it seemed impossible to alloy copper. Both metals failed to unite with tin, and while this was true of tungsten with manganese, the latter metal and molybdenum combined with apparent readiness. Cobalt, chromium, and nickel, of the seven metals whose oxides were used with the oxides of tungsten and molybdenum, seemed to alloy with the greatest ease with the tungsten and

molybdenum, yielding products which, in the case of cobalt and nickel, may prove to possess a commercial technical value, if prepared in large amounts.

A METHOD FOR THE RAPID DETERMINATION OF CARBON IN STEEL.

By Robert Job and Charles T. Davies.

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AFTER a very thorough trial of Dr. Sargent's apparatus for the rapid determination of carbon,[1] an investigation was begun with the object of retaining the continuous heating arrangement, and of reducing the apparatus to the simplest possible form without impairing in any way the accuracy of the results.

At the outset it was found that the separate, water-jacketed, copper oxide tube could be entirely eliminated by simply increasing the length of the combustion furnace to 9 inches, increasing the length of the porcelain combustion tube to 20 inches, and inserting closely rolled copper gauze about 4 inches in length, thoroughly oxidized prior to use, into the combustion tube, exactly as in the old method, placing pieces of clay-pipe stems between the copper oxide and the end of the tube in order to prevent the former from being forced out of place when the boat was run up against it in the determination.

Experiments with the furnace itself showed that three Bunsen burners each about $2\frac{1}{4}$ inches apart, having spreaders upon the tops, furnished sufficient heat to keep the porcelain tube at a bright red heat over 8 inches of its length. A thin sheet-iron shield was placed just beneath the tube as a protection from the direct action of the flame.

After the removal of the separate copper oxide tube, it was found that the gases, upon reaching the calcium chloride tube preceding the weighed bulbs, had been cooled to the temperature of the room, so that the condensing worm was no longer necessary, and further test after its removal proved that the excess of water remaining in the gas at that point was small, and was readily removed by the calcium chloride without necessity of f quent changing. It was further proved that the absorption

[1] his Journal, **22**, 277.