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CRITICAL STUDIES ON THE FUSION OF RARE METAL ORES
II. THE SEPARATION OF TANTALUM AND COLUMBIUM[1]

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In the first paper[2] of this series it was shown that titanium sulfate formed by fusion of the ore with sodium pyrosulfate decomposed into an insoluble basic sulfate if the fusion temperature reached 700°. It was pointed out at that time that similar reactions could probably be obtained in the cases of other elements occupying neighboring positions in the periodic table. Since the decomposition of titanium sulfate took place quite abruptly at 700° it seemed probable that the difference in basicity between tantalum and columbium might make possible a more complete separation than can be obtained by the methods commonly used.

Although a number of methods have been worked out for their separation, none is entirely satisfactory since all depend on relative properties that present too little difference or on conditions that are difficult to maintain. The original method of Marignac, modified by Meimberg and Winzer, which makes use of the difference in solubility of the potassium double fluorides is perhaps the most efficient. It is, however, admittedly inaccurate and effects only a partial separation, two to three precipitations being necessary to obtain tantalum free from columbium. One of the most recently developed methods[3] makes use of the solvent action of selenium oxychloride on columbium oxide, but here again the separation is not complete since tantalum oxide is also somewhat soluble.

Experimental Part

The work discussed in this paper has to do with tantalite and columbite only. All fusions were made in platinum with sodium pyrosulfate on ore ground to about 150 mesh. The ore used was a high-grade commercial product containing iron, manganese and some silica. The sodium pyrosulfate was prepared by fusing the C.P. sodium bisulfate of commerce. The general procedure was similar to that followed in the first paper.[2]

In the early part of the work the proportion of flux was varied from five to eight times that of the ore and the time of fusion ranged from 11 minutes to nearly an hour. Complete decomposition was easily obtained with the higher ratios as evidenced by the pure white color of the disintegrated melt. Considerable difference, however, was found in the solubility of the tantalum and columbium compounds formed. When the tem-

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Los Angeles, Aug. 5, 1925.

[2] Sears and Quill, THIS JOURNAL, **47**, 922 (1925).

[3] Morrill, *ibid.*, **43**, 2578 (1921).

perature was maintained just high enough to keep the mass liquid, and the heating stopped soon after the melt showed complete decomposition by the absence of solid particles floating in it, both tantalum and columbium were completely soluble in dil. hydrofluoric acid. In a number of these experiments tantalum was obtained free from columbium or columbium was obtained free from tantalum and in one case a complete separation was obtained after disintegrating the cooled melt with water and treating the residue with dil. hydrofluoric acid.

A careful study of the results obtained in these preliminary experiments seemed to indicate that the temperature at which the fusion was made had much more influence on the subsequent solubility of the tantalum and columbium compounds than either the time of fusion or the proportion of flux used. Accordingly, a series of fusions was made using seven parts of the pyrosulfate to one of ore. The temperature was measured by observing the color of the crucible through an optical pyrometer. The cooled melt was disintegrated in water and the undissolved residue, containing the tantalum and columbium, was treated with hydrofluoric acid (1:1) in a platinum dish. The solution thus obtained was tested for both tantalum and columbium as follows. The hydrofluoric acid solution was evaporated to 1–2 cc., cooled and potassium chloride solution added. A fine crystalline precipitate was taken as evidence of the presence of tantalum. If no precipitate formed, the solution was evaporated until barely moist and the residue examined under the microscope for the needle-like crystals of potassium fluotantalate, K_2TaF_7. This residue or the filtrate from the fluotantalate precipitate was then treated for columbium by making use of the change of color on reduction with zinc or tin. The reduction with tin in hydrochloric acid solution (2:1) as recommended by Moir[4] was found to be more delicate and more satisfactory and was used in all the later tests for columbium. The residue undissolved by hydrofluoric acid was fused again with pyrosulfate and tested for tantalum and columbium as outlined above. The results are shown in Table I.

TABLE I

RESULTS OBTAINED WITH HYDROFLUORIC ACID AS SOLVENT AND OPTICAL PYROMETER AS A MEANS OF OBTAINING THE TEMPERATURE OF FUSED MASS

One g. of ore and 7 g. of $Na_2S_2O_7$ were used for each fusion.

Ore	Time of fusion, min.	Pyrometer reading, °C.	Result
Tantalite	29	800	Most of Cb and no Ta dissolved
Tantalite	28	800	Most of Cb and no Ta dissolved
Tantalite	35	900	Most of Cb and no Ta dissolved
Tantalite	39	880	Most of Cb and no Ta dissolved
Columbite	40	900	Most of Cb and no Ta dissolved
Columbite	44	810	All of Cb and trace of Ta dissolved
Columbite	35	770	All of Cb and considerable Ta dissolved

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[4] Moir, *Compt. rend.*, **143,** 680 (1906).

In the last two fusions of this series the residue obtained after disintegrating the melt with water was divided into two parts and the second part was fumed with sulfuric acid, cooled and filtered through an asbestos filter. In both cases a complete separation was obtained. It appeared, therefore, that concd. sulfuric acid would make a better differentiating solvent than the hydrofluoric acid. Several difficulties attending the use of concd. sulfuric acid in this connection were soon discovered, so a number of experiments were carried out in order to determine the effect of different concentrations of the acid on the tantalum and columbium material. It was found that the concentrated acid could be diluted with about one-third its volume of water without decreasing its value as a solvent for the columbium. At the lower concentration it was somewhat less active toward the tantalum. It was also found that soluble columbium could be completely washed out of tantalum material with cold dil. sulfuric acid (approximately 6 *N*) without danger of precipitation. The hot acid, however, tends to cause precipitation of columbic acid when more than a trace is present. Table II shows the results obtained from a series of fusions in which hot sulfuric acid diluted as indicated above was used as solvent. The mixture was then cooled, filtered through an asbestos filter and the residue washed with cold dil. sulfuric acid.

TABLE II

RESULTS OBTAINED WITH SULFURIC ACID AS SOLVENT AND OPTICAL PYROMETER AS A MEANS OF OBTAINING THE TEMPERATURE OF FUSED MASS

One g. of ore and 7 g. of $Na_2S_2O_7$ were used for each fusion.

Ore	Time of fusion, min.	Pyrometer reading, °C.	Test obtained in Solution	Residue
Columbite	40	820	Cb	Ta, Cb (trace)
Columbite	49	800	Cb	Ta
Columbite	39	800	Cb	Ta
Columbite	31	800	Cb	Ta, Cb (trace)
Tantalite	38	850	Cb, Ta	Ta
Tantalite	47	850	Cb	Ta
Tantalite	38	875	Cb	Ta, Cb
Tantalite	38	875	Cb, Ta	Ta, Cb
Tantalite	31	875	Cb, Ta (trace)	Ta, Cb

The results of these experiments showed that the time of heating had little effect except as it influenced the temperature and that a more accurate means of measuring the temperature would be necessary to assure duplication of results. While under certain conditions fairly uniform results were obtained by means of the optical pyrometer, there were too many outside influences which affected the reading and made it unreliable. A platinum-nichrome thermocouple, prepared and calibrated against the melting points of tin, zinc, antimony and sodium chloride, was used in the remainder of the work.

With the ratios so far used the mass usually solidified before the final temperature was reached. Since the use of the thermocouple necessitated a liquid condition of the melt for accurate measurement, a somewhat higher ratio was necessary. A ratio of 9:1 was found satisfactory. Using this ratio a number of fusions were made at temperatures ranging from 840° to 850° with both tantalite and columbite. Complete separations were obtained in all cases.

In order to find out the range of temperature over which a complete separation would be possible and to determine whether the time of maintaining this temperature would have any effect, a series of fusions was made in which the temperature as well as the time during which a given temperature was maintained was varied. These fusions were all made with tantalite using nine parts of sodium pyrosulfate to one of ore. The results are shown in Table III.

TABLE III

DATA SHOWING THE EFFECT OF VARYING THE TIME AND TEMPERATURE OF FUSION ON THE SOLUBILITY IN SULFURIC ACID. TEMPERATURE MEASURED WITH A THERMOCOUPLE

1	Temp., °C	805	820	820	830	835	835
2	Time at temp. given, min.	20	1	5	5	10	15
3	Result, solution	Cb, some Ta;	Cb and trace of Ta;			complete sepn.	
1		835	835	850	860	875	
2		20	25	5	5	5	
3		complete separation					

It is evident from these experiments that a complete separation is possible if the fusion temperature reaches 835°. At lower temperatures some of the tantalum dissolves, although the solubility of the columbium is unaffected at temperatures as high as 875°. The time of maintaining a given temperature seemed to have little or no effect.

It is of interest to note that the separation is brought about by changes taking place in the tantalum compounds only. Although tantalum is known to form a number of complex tantalates by fusion with sodium carbonate, no study seems to have been made of the compounds formed during the pyrosulfate fusion. The acidic character of both tantalum and columbium, however, would seem to indicate the same type of compounds here also. If so, the more basic character of tantalum would make these tantalates less stable and more easily decomposed to the oxide under the influence of heat. On the other hand, if sulfates or double sulfates are formed, the columbium compounds should decompose more easily. Since the oxides of both these elements are insoluble or nearly so, it is reasonable to suppose from the results obtained that tantalates and columbates are formed by fusion with pyrosulfate. Although but little evidence can as yet be given concerning the exact nature of these compounds,[5] it

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[5] Further work is being done in this connection the results of which will appear in a later paper.

would seem probable that a tantalate containing a high percentage of sodium is first formed and that this decomposes by stages approaching the oxide as the temperature is increased. A somewhat analogous reaction is found in the decomposition of the hexatantalate, $Na_8Ta_6O_{19}$, into the meta form, $NaTaO_3$, by repeated ignition, as is also the dehydration of tantalic, columbic and tungstic acids by boiling their solutions. The formation of sodium tantalate during the pyrosulfate fusion must result in the evolution of sulfur trioxide. Its subsequent decomposition, on the other hand, should liberate sodium oxide which would react with any pyrosulfate present to form sodium sulfate and so decrease the amount of sulfur trioxide liberated. A decreasing amount of sulfur trioxide evolved, therefore, should be expected during the progress of a fusion. This agrees well with the results obtained. Although an excess of pyrosulfate was always found in the melt, the evolution of sulfur trioxide which was quite apparent during the early part of a fusion practically ceased when the higher temperatures were reached. The separation of tantalum and columbium may be assumed, therefore, to be due to the difference in decomposition temperature of the sodium tantalate and columbate formed during the pyrosulfate fusion, and to their relative solubility in concd. sulfuric acid.

The procedure finally adopted as most satisfactory was as follows. The cooled mass which had been fused at a temperature between 835° and 875° is leached with water to disintegrate the mass and remove it from the crucible. This usually requires from one to two hours. The solution is then filtered off and the residue containing all of the tantalum and columbium is washed by decantation with hot hydrochloric acid (approximately 3 N) until free from iron. Hydrochloric acid of this concentration was found to have no solvent action on either the tantalum or columbium and was more effective for removing the iron and manganese than dil. sulfuric acid. The ordinary dil. hydrochloric acid (approximately 6 N) dissolves some of the columbium. The pure white residue containing the tantalum and columbium is then transferred to a beaker, a mixture of 1:1 sulfuric acid added, the liquid covered with a watch glass and heated on a sand-bath until all evidence of boiling ceases. The cooled mixture is filtered with the aid of suction through an asbestos filter and the residue washed with cold 6 N sulfuric acid until the washing liquid gives no precipitate with ammonium hydroxide. By this process the columbium is completely dissolved while the tantalum is left in the residue.

Summary and Conclusion

A critical study of the pyrosulfate fusion of tantalite and columbite has been made and the effect of certain solvents on the product has been noted, from which the following conclusions are drawn.

1. The proportion of pyrosulfate used in the fusion mixture and the time of heating have little or no effect on the solubility of the product formed.
2. Concd. sulfuric acid is a more effective differentiating solvent for the tantalum and columbium than hydrofluoric acid.
3. A complete separation of tantalum and columbium may be obtained with concd. sulfuric acid if the fusion has been made at 835–875°.
4. The solution of columbium is unaffected by cold 6 *N* sulfuric acid but is almost completely precipitated in a hot solution.
5. The compounds formed by the fusion are probably tantalates and columbates rather than sulfates or double sulfates.
6. A method of procedure is given for the separation of tantalum and columbium.

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THE SYSTEMS FORMED BY CERTAIN INORGANIC COMPOUNDS WITH LIQUID SULFUR DIOXIDE

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In 1920 Waddell, in this Laboratory, while determining the solubilities of inorganic substances in sulfur dioxide, found that tin tetrabromide was soluble in all proportions above 49°, while below that temperature two liquid layers were obtained. The writers have investigated other tetrahalogen compounds of the same periodic group and have found that in several other cases the double layers may occur. The present investigation is concerned with those formed when stannic bromide and chloride and titanic chloride are treated with anhydrous sulfur dioxide.

The most common method for determining the mutual solubilities in binary systems was introduced by Alexejew.[2] It consists in sealing known weights of the two components in glass tubes, raising their temperature slowly while they are being agitated, and noting the temperature at which the mixture becomes clear. If the process be repeated with a series of concentrations, the complete solubility curve may be obtained. In thermostatic methods the temperature is maintained constant and the composition of the two layers is determined by analysis. The former of the two methods was used in our work.

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[1] Adapted from a dissertation presented by Howard Thomas Beach to the Graduate Faculty of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Alexejew, *Wied. Ann.*, **28,** 305 (1886).