TANTALUM AND NIOBIUM MINERALS OF INDIA

N. R. SRINIVASAN

Abstract

Two rare metals, tantalum and niobium, have received considerable attention in view of their vital importance and military applications. This paper presents a critical review of recent literature on the discovery of new minerals, exploration and production, for the minerals in many parts of the world, studies on the pure metals, their alloys and compounds. Recent work in India and the possibilities with regard to these metals in this country have been specially emphasized.

Introduction

THE two rare metals, tantalum and niobium, are now considered to be of critical importance. Extensive work has been conducted in many countries to locate new ore deposits of the metals, to prepare pure metals, alloys and compounds and to investigate their uses. In this paper an attempt has been made to review current literature critically with special reference to the minerals of tantalum and niobium in India.

Importance of the Two Metals

Tantalum and niobium were less familiar metals till recently and found only limited use. During the last few years, particularly in America, enormous work has been conducted on the metals, their alloys and compounds. It has been reported in the U.S. recently^{1,2} that tantalum and niobium figure among 'ten metals still on critical list ', and that the demand for niobium is 20 times greater than the supply. The metals have been produced by vacuum reduction³, by electrolysis of fused salts⁴ and by electrodeposition⁵. Tantalum finds innumerable applications in chemical plant equipment, where it resists

the attack of 70 common acids and other corrosive chemicals⁶. It is an integral part of electronic tubes especially for ultra-high frequencies7. It has been invaluable in surgery and in medical applications⁸. New alloys of tantalum and niobium with various metals have been developed to meet special needs. The addition of niobium and tantalum to zirconium raises the strength of elevated temperatures^{9,10}. zirconium at Titanium-tantalum alloy systems and titanium-tantalum-molybdenum alloy systems have been studied¹¹⁻¹³. The two metals have been used in welding electrodes¹⁴, in thermocouples¹⁵, for sandcasting of aluminium alloys¹⁶, in high-speed steels, and niobium in fluorescent materials¹⁷. Niobium is reputed to be vital in high-temperature alloys for gas turbine rotor blades and jet engine parts¹⁸. Lastly attention must be drawn to the separation of niobium and zirconium, and niobium and tantalum by using ion exchange resins^{19,20} and the development of a radioactive technique for the detection of tantalum in ferroniobium alloys and niobium ores²¹. Thus it will be evident that there are important uses for niobium and tantalum in many fields; however, the incorporation of niobium in jet engine alloys may outshadow its other uses and render the metal of vital significance for military applications.

Mode of Occurrence

In nature, the two metals invariably occur together as tantalates and niobates in view of their close resemblance in many of their properties. According to Clarke and Washington²², these two elements constitute 0.003 per cent of igneous rocks of the earth's crust. Though they are dispersed in about 50 rock minerals SYMPOSIUM ON NON-FERROUS METAL INDUSTRY IN INDIA

most of them are rare and only a few are of commercial significance. Since small quantities of uranium are to be found in some of their minerals, they have been extensively exploited in many parts of the world. The minerals for most part are complex and further, owing to certain erroneous conceptions which prevailed earlier, it has been stated that many of the reported formulae 'are worthless quantitatively and defective qualitatively '23. However, recent refinements in their analyses have yielded reliable The classification of the minerals can data. be done according to crystallographic characteristics or chemical composition. Dana²⁴ classifies them crystallographically as follows:

- (a) Isometric Pyrochlore group Pyrochlore, hatchettolite, microlite.
- (b) *Tetragonal Fergusonite* group Fergusonite, sipylite.
- (c) Orthorhombic Columbite group—Columbite, tantalite.
- (d) Orthorhombic Samarskite group Samarskite, yttrotantalite.
- (e) Orthorhombic Aeschynite group Aeschynite, euxenite polycrase.

They can be classified chemically as tantaloniobates and titanoniobates. The most important ones commercially are the columbite, tantalite and samarskite. There is a perfect gradation from columbite to tantalite with a corresponding increase in the specific gravity of the minerals. They usually occur in pegmatites and are black, lustrous and heavy.

New Minerals and Explorations Abroad

Some new minerals and finds of niobium and tantalum have recently been reported in literature and extensive explorations are going on for their minerals in many nations of the world. A new black mineral of the chemical composition of meta-titanate-niobate has been discovered in Japan and named Kobeite²⁵. In the United States, activity is

brisk and though columbite has been known to occur in South Dakota²⁶ and Colorado²⁷, U.S. Geological Survey currently announced fields of rich deposits in an area known as Magnet Cove in Central Arkansas²⁸. In Nigeria, where the greatest amount of tantalum-niobium minerals are produced, important occurrences of their minerals in granites and placers have been reported^{29,30}. In Belgian Congo tantalite and columbite have been noticed³¹. Tantalite occurs in minable amounts in pegmatite dykes of Karbib area in South-West Africa³². Small quantities of bismuthotantalite and other minerals have been worked in Uganda³³. The tantalite deposits of the Pilbara goldfield in Western Australia have yielded much of the minerals in that country³⁴. Brazil has exported tantalites during and after the last war^{35,36}. In Pampacolca pegmatites of Peru tantalum-niobium minerals are noticed³⁷. On the Continent, in Portugal, tantalite in the pegmatite of Mangualda was noted for the first time associated with cassiterite³⁸. Deposits of the minerals have been found in Italy³⁹, U.S.S.R.⁴⁰, Sweden⁴¹, Norway⁴², Greenland⁴³, Alaska⁴⁴ and Manchuria⁴⁵. The world production of tantalite-columbite was estimated to be about 2460 tons in 1945 by the U.S. Bureau of Mines⁴⁶. Nigeria contributed 1796 tons, while Australia, Brazil, Belgian Congo and U.S. produced 250, 200, 200 and 3.5 tons respectively. The U.S. has now fixed a long-term price for the minerals and it appears that there is no danger that the demand for niobium will drop in the near future47.

Occurrence in India

Though a regular survey for the rare minerals was not undertaken, except in the recent past by the Geological Survey of India, many occurrences of tantalum and niobium minerals have been noted in several parts of the country. The first recorded occurrence is a tantalite from Palni (Madras) by Muzzy⁴⁸. Tantalites and columbites have later been noticed in the mica-bearing pegmatites of India. Columbite was first found by French at Pananova Hill in Monghyr district (Bihar)49 and was examined by Holland⁵⁰. It has also been found in Hazaribagh district (Bihar)⁵¹ and at Masti, Bangalore district (Mysore)⁵². The author recently examined a heavy black, lustrous specimen of columbite from Coimbatore (Madras) and analysed it. Columbite has been found in association with monazite and uranium ochre in Gaya district (Bihar)53. It has also been studied recently from the pitchblende deposits of Bihar⁵⁴, in Rajasthan in association with tantalite⁵⁵ and at Othara (Travancore) as a radioactive columbite^{55a}. Samarskite is known to occur in Sankara mine. Nellore district (Andhra)⁵⁶, and in Yedur, Bangalore district (Mysore)⁵⁷. Among rare minerals, in Nellore a mineral resembling allanite containing 18 per cent Nb₂O₅ and another mineral sipylite have been noticed⁵⁸. Hatchettolite from Tovla taluq (Travancore), aeschynite and a titanoniobate allied to euxenite from Eraniel taluq (Travancore) have also attracted attention^{59,60}. Another mineral, probably hatchettolite or eudeiolite, containing 41 per cent (NbTa)₂O₅, has been observed near Vayampatti, Trichy (Madras)⁶¹. While many occurrences of these minerals have been known, production in India has been negligible. In 1937 about 12 cwt. of the minerals were worked from Bihar, in 1944 the production has been 10.5 cwt. from Mewar (Rajasthan)62 and no production has been reported in subsequent years.

Recent Studies in India

In the last few years, several Indian workers have directed their attention to the correct analyses of the minerals, separation and preparation of pure compounds of niobium and tantalum and allied studies. Six specimens of samarskite associated with columbite-tantalite and containing appreciable quantities of uranium have been analysed and found to contain 53.4-69.7

per cent (NaTa)₂O₅ ⁶³. A specimen of samarskite collected by Tipper (loc. cit.) from Nellore has now been analysed and found to contain 44.5 per cent Nb₂O₅ and 8.03 per cent Ta₂O₅⁶⁴. The preparation of pure metal oxides from Indian columbite and the analysis of binary and ternary mixtures of tantalic, niobic and titanic acids have been undertaken^{65,66}. The analytical separation of niobium and tantalum has received attention. Extensive investigations have been conducted on complex compounds of the metals resulting in the isolation of two new series of compounds called the tartratoniobates and the tartratotantalates and the preparation and physico-chemical study of 30 new complex salts and some niobates⁶⁷⁻⁷². Physical studies on the metals have revealed new bands of niobium oxide73 and a study of the energy spectrum of tantalum has also been made⁷⁴. The above only illustrates the interest on the two metals in the country.

Possibilities in India

Though recorded occurrences of the minerals of tantalum and niobium are many in India, the extent of these deposits is not known. It is believed that the Rare Minerals Section of the Indian Atomic Energy Commission is exploring the occurrences of the two metals in the country as an ancillary to a search for strategic minerals. The geological work can be complemented by work on the chemical and metallurgical aspects of the metals. In view of the importance of citrates in ion exchange, studies could be initiated on the citrate complexes of niobium The importance attached to and tantalum. the niobium alloys in the aircraft industry has been mentioned earlier. While a limited study of tantalum-titanium alloys has been made abroad, in view of our enormous resources of titanium, alloys of titanium, niobium and tantalum could be prepared and studied. The addition of niobium and tantalum to zirconium raises the strength of SYMPOSIUM ON NON-FERROUS METAL INDUSTRY IN INDIA

Zr at elevated temperatures; hence Zr-Nb-Ta alloys offer special advantages. Thus studies on the two metals niobium and tantalum will greatly help the non-ferrous metal industry and the resources of our country.

References

- 1. Mining Engineering, 5 (1953), 129.
- 2. International Chem. Eng. & Process Ind., 33 (1952), 624.
- 3. KROLL & SCHLECHTEN, J. Electrochem. Soc., 93 (1948), 247.
- 4. ANDRIEUX, J. four elec., 57 (1948), 26.
- 5. KOIZUMI, Japan Patent 172,313 (1946).
- 6. PERCY, Chem. Eng., 59 (1952), 251.
- 7. BALKE, Chem. & Ind., 83 (1948).
- 8. Olson & HOFFMANN, U.S. Patent 2,491,416 (1949).
- 9. SCHWOPE & CHUBB, J. Metals, 4 (1952), 1138.
- 10. ANDERSON et al., U.S. Bur. of Mines Rep. Invest. No. 4658 (1950).
- 11. MAYKUTH & OGDEN, J. Metals, 5 (1953), 2317.
- 12. SUMMERSMITH, J. Inst. Met., 81 (1952), 73.
- 13. Italian Patent 465,752 (1951).
- 14. Australian Patent 174,268 and 174,262 (1953).
- 15. Morgan & Donforth, J. Apply. Phys., 21 (1950), 112.
- 16. CIBULA, J. inst. of Metals, 76 (1949), 321.
- 17. WILLIAMS, U.S. Patent 2,447,927 (1948).
- HARRIS & CHILD, Iron & Steel Inst. Special Report No. 43, pp. 67, 135 and 246.
- 19. Томркіль et al., J. Am. Chem. Soc., 69 (1947), 2769.
- 20. KRAUS, J. Am. Chem. Soc., 71 (1949), 3855.
- 21. ANDRE KOHN, Compt. rend., 236 (1953), 1419.
- 22. CLARKE & WASHINGTON, Proc. Nat. Acad. Sci., 8 (1922), 112.
- HILDEBRAND & LUNDELL, As quoted from The Analytical Chemistry of Tantalum & Niobium (Schoeller, Chapman & Hall, London), (1937), 23.
- 24. DANA, System of Mineralogy, 6th Ed., New York, p. 273.
- 25. Такиво et al., J. Geol. Soc., Japan, 56 (1950), 509.
- RUNTE et al., U.S. Bur. of Mines Rep. Invest. No. 4928, (1952), 46.
- 27. WILSON & YOUNG, U.S. Bur. of Mines Rep. Invest. No. 4939 (1953), 7.
- 28. Annon, Mining Eng., 5 (1953), 662.
- 29. MACKAY et al., Br. Geol. Sur. & Museum, At. Energy Div. Rep. No. 95 (1952), 1-25.

- JACOBSON & WEBB, Geol. Sur. Nigeria Bull., 17 (1946), 51.
- MOREAU et al., Am. Soc. Geol. Belg. Gull., 73 (1950), 213.
- 32. FROMMURZE et al., Uni. S. Africa Dept. Min. Geol. Surv. No. 79 (1942), 180.
- DAVIES & BISSET, Bull. Imp. Inst., 45 (1947), 161.
- 34. FINUCAVE & TELFORD, Aer. Geol. Geoph. Sur. N. Austr. Rept. W. Sust. No. 46 (1939), 8.
- PINTO, Brazil Ministerio. Lab. Producao mineral Bol., 21 (1946), 61.
- 36. MATHIAS, Bol. Univ. Sao Paulo, No. 18 Min. 3 (1939), 51.
- 37. FREYREV, Bol. Soc. quim, Peru, 14 (1948), 1.
- 38. JESUS, Bol. Soc. portuguesa Cience nat., 13 (1942), 442.
- 39. MAGISTRETTI, Atti. Soc. Ital. Sci. nat. museo. Civico Storia nat. Minaco, 85 (1946), 136.
- 40. SEMENOV, Doklady Akad Nauk U.S.S.R., 50 (1945), 411.
- 41. SUNDIUS, Geol. Foreu, Stockholm, 72 (1950), 473.
- 42. CONRADI, Tids. Kjemi Bergveseu Met., 13 (1953), 11.
- 43. ILLINGWORTH, Min. Mag., 84 (1951), 24.
- BATES & WEDOV, U.S. Geol. Sur. Cir. No. 202 (1953), 1-13.
- 45. KUNO, Proc. Japan Acad., 22 (1946), 310.
- 46. Minerals Year Book, U.S. Bur. of Mines, 1945.
- 47. International Chem. Eng. & Process Ind., 33 (1952), 624.
- MUZZY, Catal. Govt. Centr. Museum, Madras. "Madura, Its Rocks & Minerals", (1855), 4.
- 49. FRENCH, Rec. Geol. Surv. Ind., 27 (1894), 1.
- 50. HOLLAND, Rec. Geol. Surv. Ind., 28 (1895), 10.
- 51. HOLLAND, Rec. Geol. Surv. Ind., 29 (1897), 129.
- 52. JAYARAM, Rec. Mys. Geol. Dept., 3 (1900-1), 182.
- 53. TIPPER, Rec. Geol. Surv. Ind., 50 (1919), 254.
- 54. NARAI, Ind. Minerals, 6 (1952), 65.
- 55. CROOKSHANK, Trans. Min. Geol. Met. Inst. Ind., 42 (1948), 105.
- 55a. PAULOSE, Curr. Sci., 19 (1950), 277.
- 56. TIPPER, Rec. Geol. Surv. Ind., 41 (1911), 210.
- 57. QUIN, REV., Rec. Geol. Surv. Ind., 64 (1930), 424.
- QUIN, REV., Rec. Geol. Surv. Ind., 50 (1918), 303.
- 59. QUIN, REV., Rec. Geol. Surv. Ind., 52 (1921), 308.
- 60. QUIN, REV., Rec. Geol. Surv. Ind., 48 (1917), 8.
- QUIN, REV., Rec. Geol. Surv. Ind., 41 (1911), 210.
- 62. QUIN, REV., Ind. Minerals., 2 (1948), 25.
- 63. KARUNAKARAN & NEELAKANTAN, Proc. Ind. Acad. Sci., 25A (1947), 404.

- 64. NANDI & SEN, J. Sci. Ind. Res. Ind., 7A (1948), 31.
- 65. BHATTACHARYA, J. Ind. Chem. Soc., 29 (1952), 871.
- 66. Внаттаснакуа, Sci. & Cult., 16 (1950), 69, 121.
- 67. SRINIVASAN, Proc. Ind. Acad. Sci., 31A (1950), 194.
- 68. SRINIVASAN, Proc. Ind. Acad. Sci., 31A (1950), 300.
- 69. SRINIVASAN, Proc. Ind. Acad. Sci., 31A (1951), 381.
- SRINIVASAN, Proc. Ind. Acad. Sci., 36A (1952), 185.
- 71. SRINIVASAN, Proc. Ind. Acad. Sci., 36A (1952), 278.

- 72. SRINIVASAN & VENUGOPALAN, Curr. Sci., 20 (1951), 205.
- 73. RAO RAMAKRISHNA, CUVY. Sci., 18 (1949), 168.
- 74. JNANANDA, J. Sci. Ind. Res. Ind., 8B (1949), 148.

Discussion

DR. H. BHATTACHARJEE (National Metallurgical Laboratory, Jamshedpur)

Commenting on the paper stated that regarding the exact composition of the minerals of niobium and tantalum in India, it is believed that the minerals are mainly niobates, though some tantalite has been found at Jhajha in Bihar.

#