High purity thorium metal powder was repetitively produced in a laboratory cell and in an expanded scale electrolytic cell by electrolysis of this cell feed. The thorium metal produced was readily compacted, arc-melted, and rolled. Thorium metal ingots with as-cast hardnesses of R_B 5 (Vhn 68) were produced.

The preparation of thorium chloride, descriptions of both electrolytic cells, and some properties of the produced electrolytic thorium metal are given. A bibliography of other processes, electrolytic and nonelectrolytic, for the production of thorium metal is included.

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References

- ¹ A. Atanasin and M. Babor: *Bulletin de chimie pure et appliquée de la société roumaine de chimie*, 1935-1936, vol. 38, pp. 83-90.
- ² J. J. Berzelius: *Pogg. Ann.*, 1829, vol. 16, p. 385.
- ³ A. S. Cachiemaille: British Patent No. 238,347, 1924.
- ⁴ A. S. Cachiemaille: British Patent No. 233,470, 1924.
- ⁵ E. Chauvenet: *Comptes rendus*, 1909, vol. 14, pp. 1267 and 1519.
- ⁶ A. Cotellie and M. Haissinsky: *Comptes rendus*, 1938, vol. 206, pp. 1644-1646.
- ⁷ F. H. Driggs and W. C. Lilliendahl: *Industrial and Engineering Chemistry*, 1930, vol. 22, No. 12, p. 1302.
- ⁸ O. Honigschmidt: *Comptes rendus*, 1905, vol. 142, pp. 157 and 280.
- ⁹ W. Huppertz: *Chemisches Zentralblatt*, 1904, vol. 1, p. 1383.
- ¹⁰ G. E. Kaplan: Metallurgy of Thorium. Geneva Conference, 1955.
- ¹¹ K. Koizumi et al.: Japan Patent No. 172,315, 1946.
- ¹² H. Kuzel and E. Wedekind: U. S. Patent No. 1,088,909, 1914.
- ¹³ R. Lautie: *Bulletin de la société chimique de France*, 1947, vol. 14, pp. 974-977.
- ¹⁴ W. C. Lilliendahl: U. S. Patent No. 2,537,067, 1951.
- ¹⁵ J. W. Marden: U. S. Patent No. 1,437,984, 1923.
- ¹⁶ J. W. Marden, E. Conley, and T. P. Thomas: U. S. Patent No. 1,487,174, 1924.
- ¹⁷ J. W. Marden: U. S. Patent No. 1,648,954, 1927.
- ¹⁸ J. W. Marden: *Trans. Electrochemie Soc.*, 1936, vol. 66, p. 39.

- ¹⁹ G. A. Meerson: Powder Metallurgy of Thorium. Geneva Conference, 1955.
- ²⁰ H. Moissan and A. Etard: *Comptes rendus*, 1896, vol. 122, p. 573.
- ²¹ H. Moissan and A. Etard: *Annales de Physique*, 1897, vol. 12, No. 7, p. 427.
- ²² H. Moissan and O. Honigschmidt: *Annales de Chimie et de physique*, 1905, vol. 8, No. 7, p. 182.
- ²³ R. Piontelli and A. Bulloito: *Chimica e industria*, 1939, vol. 21, pp. 478-491.
- ²⁴ H. C. Rentschler, W. C. Lilliendahl, and J. E. Grey: U. S. Patent No. 2,446,062, 1948.
- ²⁵ H. Schlect and M. Jahrstofer: U. S. Patent No. 2,242,759, 1941.
- ²⁶ M. A. Steinberg, M. E. Sibert, and E. Wainer: *Journal Electrochemical Soc.*, 1954, vol. 101, p. 63.
- ²⁷ A. E. Van Arkel: *Reine Metalle*, p. 213. J. Springer, Berlin, 1939.
- ²⁸ H. Von Wartenburg, J. Bray, and R. Reinicke: *Ztsch. für Electrochemie*, 1933, vol. 29, p. 214.
- ²⁹ Westinghouse Electric International Co.: British Patent No. 623,160, 1949.
- ³⁰ C. Winkler: *Berichte*, 1891, vol. 24, p. 873.

Discussion of this paper sent (2 copies) to AIME by Jan. 1, 1958 will appear in AIME Transactions Vol. 212, 1958, and in JOURNAL OF METALS, October 1958.

Technical Note

On Complex Formation in the System $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$

by Tormod Forland

FROM equilibrium measurements on the system $\text{NaF-Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3\text{-Na}_2\text{CO}_3\text{-CO}_2$ with high contents of NaF, Forland, Storegraven, and Urnes¹ concluded that complexes are formed containing two oxygen, three aluminum, and a less defined number of fluorine per complex. The same number of oxygen atoms per complex was also found by cryoscopic measurements for mixtures high in Na_3AlF_6 .

In a recent paper by Stokes,² some other complex ions, $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ and AlOF_2^- , have been suggested.

Here an additional argument in favor of the complex $\text{Al}_3\text{O}_2\text{F}_6$ suggested by Forland, Storegraven, and Urnes will be given.

When fused Na_3AlF_6 containing some Al_2O_3 is cooled slowly, the solid phase will consist of the two components as separate phases. The melting point and the heat of fusion of Al_2O_3 are so high that this component will form the stable solid phase even though in the liquid state the complex may have a high stability. If, however, the fused mixture is quenched, the decomposition of the oxygen-containing complex and the formation of solid Al_2O_3

does not proceed fast enough, and a solid solution of Al_2O_3 in Na_3AlF_6 is obtained. Zintel and Morawietz³ obtained cryolite containing 10 pct Al_2O_3 in this way. The density and the lattice parameters of the Al_2O_3 containing cryolite were also measured, and from this it was concluded that the Al_2O_3 enters the cryolite lattice as Al_3AlO_6 groups replacing Na_3AlF_6 groups. However, the experimental data could as well be explained by assuming that one Na^+ ion and two of its neighboring F^- ions are replaced by one Al^{3+} ion and two O^{2-} ions. This may be pictured schematically as:

This means that the complex in the solid solution, derived from X-ray and density measurements, is the same as that which Forland, Storegraven, and Urnes derived from equilibrium measurements in the liquid state.

References

- ¹ T. Forland, H. Storegraven, and S. Urnes: *Ztsch. für anorganische und allgemeine Chemie*, 1955, vol. 279, p. 205.
- ² J. J. Stokes: *AIME Trans.* To be published.
- ³ E. Zintel and W. Morawietz: *Ztsch. für anorganische und allgemeine Chemie*, 1939, vol. 240, p. 145.

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