



ISSN: 2321-4902

Volume 1 Issue 2

Online Available at www.chemijournal.com

International Journal of Chemical Studies

Issues and Challenges in the Preparation of Niobium for Strategic Applications

T. Satish kumar ^{1*}, T. Balaji ¹, S. Rajesh kumar ¹, Arbind kumar ¹, T. L. Prakash ¹

1. Nano Refractory Metals Division Centre for Materials for Electronics Technology, IDA Phase-III, Cherlapally, Hyderabad – 500 051, India.
[E-mail: satish0403@gmail.com; Fax: +91-40-27261658]

Niobium is well known refractory metal having high melting point (2468 °C) and boiling point (4742 °C). Owing to its corrosion resistance at high temperature with relatively lower density, it is a preferred material for space applications. One of the most crucial applications of Nb has been found in aviation and aerospace industry where Nb based alloys are being used in a big way in rocket nozzles, rocket thrusters, satellite antennae, etc. In addition, Niobium in the form of powder is widely used in the fabrication of solid electrolyte capacitors. Although the reduction process is reported and commercialized, in the present paper few attempts are made to study the process parameters to obtain higher niobium yield, purity and economically viable process. It is reported that the yield of niobium depends up on the temperature, purity of niobium pent oxide, aluminum content and refractory lining thickness of crucible.

Keyword: Niobium pentoxide, Aluminothermic Reduction, Refractory Lining, and Niobium.

1. Introduction

The three familiar niobium metal oxide reduction processes are calciothermic reduction^[1-2], aluminothermic reduction^[3-10], and magnesiothermic reduction^[11] and magnesium vapor reduction process^[12]. In calciothermic reduction, niobium oxide is reduced with calcium in the presence of iodine/sulphur as a thermal booster. This process can be applied in order to obtain small quantities of fairly pure solid metal. In magnesiothermic reduction, the reduced metal will be in the form of powder with 0.5-4% oxygen impurities. The other important way of metal oxide reduction is aluminothermic reduction process. The metallothermic reduction of niobium oxide with aluminum is the most economically viable process for producing niobium metal. The raw material for producing niobium metal is high purity niobium oxide which is prepared through solvent extraction and calcination processes. Metallothermic reduction

is carried-out at a temperature (nearly 2050 °C) where the metal and slag get proper separation in the molten condition. The reduction reaction is exothermic (Free energy is -925 KJ/mol Nb_2O_5) and the heat generated is sufficient for the completion of reduction. In the present paper different batches of aluminothermic reduction experiments are studied by changing aluminum content, refractory crucible wall thickness.

2. Experimental

2.1 Ore dissolution

Columbite-Tantalite ore is used as raw material for the preparation of niobium. The ore is ground to fine powder by series of crushing and milling operations using Jaw Crusher, Roll Crusher and Pulveriser. The ore powder is dissolved in hydrofluoric acid in the presence of steam.

2.2 Solvent Extraction and Niobium Pent-oxide Preparation ^[13]: This is very critical stage

in niobium oxide preparation. At this stage the niobium is separated from the other constituents like tantalum, iron, etc. Feed, scrub & strip solutions are prepared and subsequently passed through mixer settler boxes for the separation of tantalum. After tantalum extraction, pH of the Feed raffinate solution is increased by passing ammonia gas. The feed raffinate precipitate is dissolved in 40% hydrofluoric acid and sulphuric acid is added to maintain the free acid concentration of 5N HF and 9N H₂SO₄. The total niobium content of the solution is maintained at 125-150 g/L. Equal volumes of tri-butyl

phosphate and kerosene is mixed to prepare organic solvent and equilibrated with 5N HF. The niobium is precipitated as niobium hydroxide at 6-6.5 pH. The precipitated is allowed to settle and the supernatant liquid is decanted. The precipitate is further washed with water to remove soluble impurities. Niobium hydroxide is calcined at 700 °C for a couple of hours and niobium pent oxide prepared. The phase purity of niobium pent oxide is confirmed by XRD studies as shown in Fig. 1.

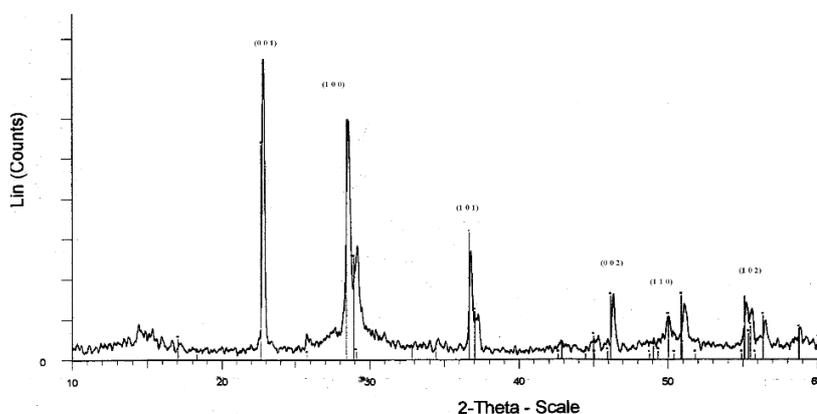


Fig 1: XRD spectrum of phase pure niobium pentoxide

2.3 Aluminothermic Reduction of Niobium pentoxide

The metallothermic reduction of niobium oxide with aluminum is the most preferred method for the production of high purity niobium metal. Reduction is carried out in ceramic (alumina) vessels at elevated temperatures. Usually these vessels will be used once and destroyed after the reaction over for the separation of niobium metal and resulted slag. Different batch sizes of (200 gm to 1.5 Kg of niobium pent oxide) aluminothermic reduction experiments are conducted and the results are studied.

2.3.1 Reduction Process: Initially the refractory cement lined MS crucible is placed in the furnace and heated up to 900 °C for two hours and allowed for cooling. Required quantity of niobium pent oxide is placed in the tray and kept in oven at 50 °C for two hours to remove the moisture. As per the reduction equation (Equation

1) the aluminum powder quantity taken and mixed with niobium pent oxide and loaded into crucible. While loading the reaction mixture, potassium perchlorate (booster) also added carefully to generate required heat during experiment. To initiate reduction reaction, little quantity of magnesium powder is spread on the reaction charge and fired with the help of magnesium wire. Fig. 2 shows the reduced niobium mass along with slag in molten condition.

After cooling the reduction charge to room temperature, the crucible is broken and solid niobium is separated from the slag material. After removing the slag, the reduced mass is hydrided and converted into 2 to 3 cm size chunks and afterwards same material is dehydrided to remove hydrogen. These metal pieces are used as feed for electron beam melting.



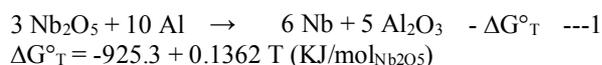
Fig 2: Molten charge after aluminothermic reduction process

2.4 Electron Beam Melting and Ingot Preparation

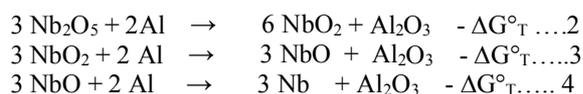
Dehydried niobium chunks are melted in a 60 KW electron beam melting (EBM) system (LEW make, Germany). After EB melting the niobium chunks, the yielded niobium metal ingot weight is 80% that of feed Nb weight. For further purification, the EB melting process is repeated. The final niobium ingot is analyzed for its chemical and gaseous impurity contents.

3. Results and discussion

The reduction of Nb_2O_5 by aluminum follows the following formula:



The reduction of niobium oxide by aluminum do not complete in one step but in several steps via niobium sub-oxides.



The amount of free energy is an indication for the stability of a chemical compound. It is reported

that the compound NbO is the most stable compound in the above system. Therefore, the losses of niobium in the slag have to be as NbO. The equilibrium of the metallothermic reduction of niobium oxide by aluminum will be controlled by equation 4. The equilibrium can be described with the following equation:

$$K_p = \frac{N_{\text{Nb}}^3 + N_{\text{Al}_2\text{O}_3}}{N_{\text{NbO}}^3 + N_{\text{Al}}^2}$$

From the above equation it can be observed that the content of NbO in the slag is dependent on temperature and the aluminum content. The maintenance of temperature during reduction reaction is difficult as it is an exothermic reaction. The only way to control temperature is to alter aluminum content and perfect sealing of refractory crucible. In order to see the effect of refractory cement wall thickness of reduction crucible, few reduction experiments conducted with different wall thicknesses (1 to 4 cm). It was observed that 4 cm wall thickness gave higher reduction mass that of others. The addition of excess aluminum content also varied from 5% to 10% more than stoichiometric and niobium metal yield was observed. It was found that 8% excess aluminum addition yields higher reduction mass compared to others. With 8% excess aluminum addition, different batch reduction experiments (200 gm – 1500 gm niobium pent oxide) are conducted in 4 cm thick refractory crucibles. The chemical analysis of 1500 gm niobium oxide reduction experiment is given in Table 1.

Table 1: Chemical analysis (in ppm) of aluminothermic reduced and electron beam refined niobium metal samples

Before electron beam refining			After Electron Beam refining	
Element melting	Impurities	Max. limit	First melting for EBM *	Second
Al	3.98%	Up to 6 %	110	<10
Fe	1860	3000	<500	<10
Ni	196	--	<10	<10
O	4600	7000	760	250
C	250	--	13	25
H	10	150	5	<5

*Technical brochure of M/s ALD Vacuum Technologies, Germany

The reduced metal yield of above experiments is also found in the range of 93 to 95% after subtracting the impurity values. In order to get high purity niobium ingot, the dehydrated niobium pieces are electron beam (EB) refined. Prior to EB melting the reduced mass is hydrided to get brittle form and broken into 2-3 cm size pieces suitable to EB system feeding. Hydriding of niobium is done in an inconel retort under ultra pure hydrogen gas between 400 °C to 900 °C. Dehydrating treatment of broken niobium metal pieces is carried out at 700 °C under high vacuum conditions (10^{-6} Torr) in an inconel retort. Prior to electron beam melting the dehydrated niobium metal is analyzed for hydrogen content and found 10 ppm which is acceptable for EB melting feed. Melting and refining process of above niobium metal is done in the 60 KW electron beam melting system. Initially one melting run is done and analyzed for the impurities as shown in Table 1. It is noticed that the impurity contents are high after single melting and decided to do one more melting. Since there is no provision for feeding ingot directly in to the EB melting system again hydriding and dehydrating processes are employed to get feed chunks. After second EB melting, the impurity analysis shows that the niobium ingot is pure compared to single melting process.

4. Conclusion

In aluminothermic reduction of niobium experiments, excess aluminum content and perfect refractory crucible sealing help for getting higher niobium yield and lower impurities. Minimum two EB melting processes are required for achieving metallurgical grade niobium metal ingot.

5. References

1. Guptha CK, Jena PK. Preparation of niobium (columbium) pent oxide Trans. TME-AIME 1964; 230:1433.
2. Sehra JC, Bose DK, Jena PK. Preparation of niobium and tantalum powders by calciothermic reduction of their pent oxides. Trans Ind Inst Metals 1968; 21:21.

3. Kamat GR, Guptha CK. Open aluminothermic reduction of columbium (niobium)pent oxide and purification of the reduced metal. J Metals 1971; 2:2817.
4. Wilhelm HA, Schmidt FA, Ellis TG. Columbium metal by aluminothermic reduction of niobium pentoxide. J Metals 1966; 18:1303.
5. Guptha CK, Jena PK. high purity niobium through aluminothermic reduction of niobium pentoxide. Trans Ind Inst Metals 1969; 22: 51.
6. Kamat GR, Guptha CK. Open aluminothermic reduction of columbium pent Oxide and purification of the reduced metal. Metal Trans 1971; 2:2817.
7. Narayanan C, Mukharjee TK, Bose DK, Guptha CK. Pilot plant production of niobium metal. Trans Ind Inst Metals 1977; 30:387.
8. Mendes MWD, Santos ACP, Medeiros FFP, Alves C, Da Silva AGP, Gomes UU. Aluminothermic reduction of niobium pentoxide in a hydrogen plasma furnace. Materials Science Forum 2006; 514:599
9. Nunes CA, Pinatti DG, Robin A. Nb-Ta alloys by aluminothermic reduction of Nb₂O₅/Ta₂O₅ mixtures and electron beam melting. International Journal of Refractory Metals and Hard Metals 1999; 17:305
10. Lazzari CPD, Cintho OM, Capocchi JDT. Kinetics of the Non-Isothermal Reduction of Nb₂O₅ with Aluminium. ISIJ International 2005; 45:19.
11. Toru H. Okabe, Iwata S, Imagunbai M, Maeda M. Production of Niobium Powder by Preform Reduction Process Using Various Fluxes and Alloy Reductant. ISIJ International 2004; 44(2):285-293;
12. Kumar TS, Kumar SR, Rao ML, Prakash TL. Preparation of niobium metal powder by two stage magnesium vapor reduction of niobium pentoxide. Journal of Metallurgy, In Press
13. Mayorov VG, Nikolaev AI. Solvent extraction of niobium (V) and tantalum(V) from fluorometallate acid solutions. Hydrometallurgy 1996; 41:71.