Research Article

Preparation of Niobium Metal Powder by Two-Stage Magnesium Vapor Reduction of Niobium Pentoxide

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Magnesium vapor reduction of niobium pentoxide was studied using a laboratory system. Niobium powder was prepared by the magnesium vapor reduction at 1123 K for 5 hours and it contained about 8 mass % oxygen. However, the oxygen concentration could be decreased to 0.65% when it was prepared by double-step reduction by magnesium vapor and a chemical treatment. Controlled and diluted supply of magnesium vapor to the reaction front has averted excess heat generation at the reaction front and thereby fine particles were produced. Effects of various factors on the vapor reduction process were studied and discussed.

1. Introduction

Extractive metallurgy of niobium has attained immense academic interest [1–14], mainly due to its application in the emerging niobium and its niobium oxide electrolytic capacitors and also in the superconducting radio frequency cavities for particle accelerators, also used in mint metal [1]. Reductants such as aluminum and calcium are used for the preparation of niobium metal from its oxide [2–5]. Niobium metal and its alloys such as ferro niobium and nickel niobium alloys are being commercially produced by aluminothermic reduction process. High purity niobium metal is prepared by electron beam melting and refining of the niobium metal which is obtained from the aluminothermic reduction of its oxide [2]. Carbothermic process can be considered as another process exploited for its commercial production [6]. Awasti prepared niobium by silicothermic reduction of niobium in ultrahigh vacuum [7]. These processes result in the formation of chunk lets and coarsened powders and hence may not be useful in the preparation of fine niobium metal powder. However, requirement of niobium metal powder with stringent purity specifications for its possible use in electrolytic capacitor has necessitated the development of new techniques. Niobium metal powder is generally prepared by hydriding, crushing of niobium hydride, and dehydriding

[8]. It is reported that niobium metal powder is prepared from its oxide by calcium using electron-mediated reduction process [9]. Similar to tantalum, niobium fine powder is also prepared by liquid-liquid reduction of K_2NbF_7 with sodium [10, 11]. Niobium metal powders can be also prepared by using magnesiothermic reduction process [12–14]. Using a cyclone separator assembly, niobium is prepared by the reaction between the magnesium vapor and niobium oxide [12]. Okabe reported a preforms reduced process (PRP) for niobium metal using magnesiothermic reduction process [13].

There are a number of factors to be considered for the selection of a reductant in a metallothermic reduction. In order for a metal M^* to reduce the MO_x , the M^* must have a greater affinity with oxygen than M :

From the free energy in thermodynamic database [15] as listed in (Table 1), it is found that calcium, magnesium, and aluminium have more affinity to oxygen than the niobium. Calcium has high reactivity for the reduction of niobium oxide to niobium. However, magnesium has an advantage over calcium that it has a high vapor pressure (0.078 bar) even at moderate temperature of 1123 K. Due to this, adequate

FIGURE 1: Schematic representation of magnesium vapor reduction system.

TABLE 1: Free energy of formation of some oxides at 298 K [15].

Metal oxides	ΔG_{298}° (kJ/g-atom of O)
MoO ₃	-229
FeO	-245
WO ₃	-254.1
Nb ₂ O ₅	-353.6
Ta ₂ O ₅	-390
MgO	-568.4
CaO	-597.7
Al ₂ O ₃	-526.7

control over the reaction conditions is possible for the reduction of niobium oxide with magnesium vapor. Stefan had overcome these problems by controlling the feed and gas flow rates and obtained fine powders. However, niobium metal prepared by the cyclone reduction techniques has resulted in high concentration of oxygen (7.68%) [12].

There are not many studies reported in the literature on the preparation of phase pure niobium metal powder by magnesium vapor reduction of niobium oxide. In this work, an attempt has been made to prepare the niobium metal powder with lower oxygen content using the magnesium vapor reduction process. Influence of various factors in the magnesium vapor reduction of niobium oxide and deoxidation of niobium metal powder in a two-stage reduction process using a simple laboratory system are discussed.

2. Experimental Studies

2.1. Raw Materials. Magnesium metal turnings (99% purity, S.D. Fine chemicals), hydrochloric acid (GR grade, Merck), niobium pentoxide (>99% pure), and argon gas (UHP grade) are used for the reduction experiments. Niobium pentoxide is prepared from Indian columbite-tantalite ore (AMD, India) by solvent extraction and calcination process [16].

2.2. Magnesium Vapor Reduction Setup. A laboratory system was fabricated for the reduction experiment and the schematic sketch is shown in Figure 1. The reaction chamber is a SS430 cylindrical vessel with a lid, an inlet port, and distributor for argon gas. At the bottom of the reaction chamber, magnesium turnings are kept in a crucible. The niobium oxide compacts are filled in another crucible with perforated bottom and placed at the middle of the chamber. Both crucibles are also made up of SS430. The reaction chamber is further housed in a retort which is placed in a furnace.

Niobium pentoxide powder was compacted to pellets at a pressure of 2.94 bar with a green density of 1.2 g/cm³. Batch size of 200 g niobium pentoxide was used for the experiments and a soaking time of 5 hours was set at 1123 K. Magnesium metal turnings are taken in the 1:1 ratio by weight with respect to niobium oxide. Reactor chamber is evacuated (10⁻³ bar) and filled with argon gas (0.98 bar) to remove the atmospheric air and to create the inert atmosphere in the chamber. This process is repeated for four times. Continuous

flow of argon is adjusted to 1-2 liter/minute and maintained throughout the experiment. The temperature of the system is increased from room temperature to 1123 K. Magnesium vapor generated at the bottom crucible is diluted with the argon gas which acts as a carrier gas. Magnesium vapor with carrier gas enters into the top crucible through the perforated bottom and reacts with niobium oxide. As the by-product of the reaction, MgO , is not volatile, an increase in the weight of the product is observed. Based on this increase in weight, the percentage of reduction is calculated. After soaking at the required temperature and time, the reaction chamber is allowed to cool to room temperature while continuing the argon flow. Air is slowly introduced to the system to passivate the reduced mass. The reduced mass is transferred to a beaker containing water, and it is treated with 20% hydrochloric acid. The resultant powder is washed with distilled water, filtered, and dried at 373 K in vacuum oven (10^{-3} bar). For the second stage reduction, the powder obtained from first reduction is compacted and repeated the vapor reduction process with magnesium under the same inert atmosphere and followed by chemical treatment process. The powder thus obtained was soaked in dilute hydrofluoric acid (1% solution) for 15 minutes and washed with water, filtered, and dried under vacuum. Elemental analysis of niobium powder is carried out by Inductively Coupled Plasma Optical Emission Spectroscopy using JY2000. Scanning electron microscopy studies were performed by using Philips XL 30 microscope. The powder X-ray diffraction (XRD) patterns of samples were obtained using a Panalytical X'pert ($\text{Cu K}\alpha = 0.1542 \text{ nm}$) X-ray diffract meter. Oxygen content of the niobium powder is analyzed by O-N analyzer using inert fusion technique using LECO TC-236. Particle size analysis is carried out by Microtrac laser diffraction particle size analyzer.

3. Results and Discussions

When magnesium vapor reduction experiments were conducted for niobium pentoxide pellets of uniform size (5 mm diameter and 5 mm thickness) at 1123 K, it is observed that, with the increase in the soaking time, the weight of the product increased. Magnesium vapor reacts with niobium pentoxide and the products are niobium metal and magnesium oxide. The relation between soaking time and weight gain is shown in Figure 2. There is a weight gain of 20% for the first hour of soaking which is further increased to 43%, 45%, and 46% when soaking time increased to 4, 5, and 6 hours respectively. This shows that magnesium vapor reduction of niobium oxide depends on the time of soaking. Magnesium vapor initiates the reaction at the exterior surface of the compacts and further percolates into the interior of the pellets. The rate of reaction of niobium pentoxide with magnesium is controlled by the rate of diffusion of magnesium vapors and depends on soaking time. In another experiment, pellets with different diameters were used for the reduction experiment, where it was observed that pellets with larger diameter are not fully converted to metal even after 5 hours of soaking at 1123 K. Therefore, the pellet size also plays an important role in the rate of reaction. The photograph

FIGURE 2: Effect of soaking time on the weight of the product at 1123 K.

FIGURE 3: Lateral cross-section of the niobium pellet (15 mm diameter) after reduced at 1123 K for 5 hours.

of a lateral cross-section of a 15 mm thick niobium pellet after a reaction time of 5 hours is shown in Figure 3. The exterior portion of the pellet is black in color whereas the interior portion is still white in color. There is a bluish tinge at the interface. White color in the interior portion indicates unreacted niobium pentoxide indicating that the magnesium vapor has not diffused into the region. The black portion at the exterior portion indicates that the reaction starts at the outer surface.

Powder XRD pattern of niobium powder obtained after the first stage of magnesium vapor reduction of 5 mm pellets soaked at 1123 K for 5 hours is shown in Figure 4. It shows that, though niobium pentoxide is reduced to niobium metal, the reduction is not completed because there are significant peaks corresponding to niobium dioxide. It also shows the peaks corresponding to magnesium oxide present in the reduced mass, formed as a result of reduction of niobium pentoxide. The presence of niobium dioxide is further confirmed by

FIGURE 4: XRD pattern of niobium powder after the first stage of magnesium vapor reduction process.

TABLE 2: Chemical analysis of magnesium vapor reduced niobium powders (in ppm).

Element	Niobium pentoxide	1st stage niobium powder	After 2nd stage niobium powder
Ni	<20	35	35
W	420	550	555
Ta	925	1150	1160
Co	<20	<20	<20
Cr	<20	<20	<20
Mn	<10	<10	<5
Mg	<20	1200	925
O	—	8%	6500
Fe	<20	<20	<20

the oxygen analysis. Oxygen content of the reduced mass leached with HCl is as high as 8% (Table 2). There are no peaks corresponding to magnesium niobate as reported in earlier works [12].

Powder XRD pattern of the dried niobium metal powder obtained by the second reduction step followed by leaching with HCl and treatment with 1% HF is shown in Figure 5. This pattern is exactly matching to standard XRD pattern of niobium metal (JCPDS card no. 035-0789). Niobium dioxide peaks observed for single-stage reduced powder are completely absent in this pattern. It shows a complete reduction of oxide to metal. Further magnesium oxides peaks are also absent in the pattern as magnesium and magnesium oxide from the reduced mass are completely leached from the reduced mass. Lower concentration of oxygen is also achieved by the second-stage magnesium vapor reduction (Table 2). Fine metal powders are found to take up oxygen during powder-processing steps. Oxygen is chemisorbed into the fresh surface of metal powder, which further diffuses into the bulk during heat treatment steps [17]. In this work, a washing procedure was adopted, where niobium metal powder obtained by the second stage of reduction and leached

FIGURE 5: XRD pattern of niobium powder after double-stage reduction with magnesium vapor.

FIGURE 6: SEM micrograph of niobium powders obtained after two stage reduction.

with HCl is soaked with dilute hydrofluoric acid (1% solution) further washed with water, and dried under vacuum. Surface oxygen was removed during this process and hence resulted in low oxygen content in the metal powder, as low as 0.65%. Chemical analysis shows that there is no appreciable increase in the concentration of iron, chromium, and nickel contents in niobium metal powder (Table 2). Chances of getting contaminated from magnesium are also very little as magnesium vapor leaves behind the impurities associated with in the bottom crucible. Magnesium oxide and magnesium from the second-stage reduced mass are leached out with hydrochloric acid treatment, and magnesium content in the niobium powder is ~900 ppm.

SEM micrograph of the niobium powder is shown in Figure 6. Fine niobium powder of <1 μm particles is agglomerated from 5 to 10 μm. The absence of coarse microstructure reveals that there is no uncontrollable reaction. Magnesium vapor is diluted with the fact that carrier gas argon percolates the niobium pentoxide bed and undergoes the reaction. As the magnesium supply is very limited, heat generated in a given time is also limited. This combination of factors such as limited and dilute supply has resulted in fine and uniform powders.

The average particle size of the niobium pentoxide is 25 microns as measured by using laser beam technique

FIGURE 7: Particle size analysis of niobium pentoxide powder.

in a wet particle size analyzer as shown in Figure 7. The green density of the niobium oxide is varied from 1.3 to 1.5 g/cm³. The pellets are broken into small pieces during the reaction. The reaction front proceeds via niobium pentoxide to niobium dioxide and to niobium metal. The reduction of oxide starts at the surface of the oxide pellet. Magnesium had to diffuse through the reduced mass consisting of niobium dioxide, niobium, and magnesium oxide to the inner surface of the porous bed of unreduced niobium pentoxide. The presence of unreacted magnesium also contributes to the weight of the reduced mass. This is reflected in the presence of 8% oxygen (Table 2) in the niobium metal prepared after first stage of reduction for 5 hours soaking even though weight enhancement is >45%, which is an index of complete reduction. Second-stage reduction has resulted in pure niobium metal, without any traces of oxides. Chemical treatment of the resulted niobium powder removed the surface oxygen chemisorbed into the surface and resulted in oxygen content of 0.65%. This work proves that, using simple laboratory system, niobium pentoxide can be reduced to niobium metal powder with low oxygen content using two-stage vapor reduction technique. From the chemical analysis, it is observed that impurities like Fe, Co, Cr, Ni, and Na did not increase even after the two stages of reduction process. Hence, the purity of the raw materials is an important factor for future applications of the product. After the reduction, the particle size of the product is observed in submicron range and ultimately the surface area increases. This can enhance the charge storage capacity per gram for electrolytic capacitors.

Thus, these results show that the reduction of niobium pentoxide to niobium metal is a two-step process. First step involves the reduction of niobium pentoxide to niobium metal and niobium dioxide and the second step involves the reduction of niobium dioxide also to niobium by the repeating the same process. Similar process may be utilized for the preparation of fine powders of various metals including tantalum. Powders thus produced by this technique can be utilized for metallurgical or electrical applications.

4. Conclusion

A simple laboratory system is fabricated for magnesium vapor reduction of niobium pentoxide to niobium metal powder by using the two-stage reduction by magnesium

vapor. This system is successfully used in the preparation of high-quality niobium metal powder having fine and uniform microstructure with oxygen content as low as 0.65%. Powders thus produced by this technique can be utilized for metallurgical or electrical applications.

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