Preparation Of Niobium-Aluminium Alloys by Aluminothermic Reduction of Nb_2O_5

J.M. Juneja*

Materials Processing Division, Bhabha Atomic Research Centre,
Trombay, Mumbai - 400 085, India.

ABSTRACT

Preparation of niobium-aluminium (Nb-Al) alloys was investigated by open aluminothermic reduction of Nb_2O_5 using lime based slags. The influence of various process variables such as (i) the amount of Al in the charge, (ii) slag composition, (iii) use of heat energiser ($KClO_3$ + Al) etc. was studied to establish conditions for good slag-metal separation and also to achieve optimum recoveries of the alloys. Alloys containing 54 to 92 % Nb could be obtained by this route. Whereas the aluminium rich alloys ($NbAl_3$) were obtained at a maximum recovery of ~ 98 %, the yield of Nb - rich alloys (Nb-Al solid solution) was over 84 %. While the $NbAl_3$ alloys were found to contain 54.6 % Nb, 45.2 % Al, 0.516 % oxygen and 0.009 % nitrogen, the Nb-rich alloys analysed 92.3 % Nb, 4.5 % Al, 0.084 % oxygen and 0.004 % nitrogen.

INTRODUCTION

Niobium aluminides are potential materials for high temperature structural applications in the aircraft and spacecraft industries /1,2/. The $NbAl_3$ phase is a promising material /3/ for high temperature applications because of its low density ($4.54x10\ ^3 kg/m^3$), high melting point (1953K), good oxidation resistance and ordered DO_{22} crystal structure for creep resistance. The intermetallic compound Nb_3Al has also received attention both as a high temperature structural material as well as a superconducting material /4,5/. The addition of niobium to titanium-aluminium (Ti_3Al) alloys imparts ductility /6,7/ needed to fabricate this material for the aircraft and spacecraft industry. The niobium-rich alloys are also useful for preparation of high purity niobium metal by electron beam melting /8/ or fused salt electro-refining /9/. The niobium aluminium alloys are thus of commercial interest over the entire composition range.

The Nb-Al binary alloy system /10/ involves the formation of three intermediate phases, namely Nb_3Al, Nb_2Al and $NbAl_3$ in addition to the terminal solid solubility regions. Whereas the Al-rich $NbAl_3$ phase has a very narrow composition range (line compound), the Nb_3Al and Nb_2Al phases demonstrate wide homogeneity ranges. The maximum solid solubility of Al in Nb is 21.5 at. pct. at the peritectic temperature of 2333K and 9 at. pct. at 773K. The solid solubility of Nb in Al is however negligible.

The Nb-Al alloys can be prepared by arc melting or reactive sintering of constituent metals /11,12/. However, these processes require the use of costly niobium metal which is produced by energy intensive routes. Calciothermic reduction of Nb_2O_5 in presence of aluminium /13/ has been reported for the preparation of Nb-Al alloys. However, the relatively high cost of calcium, the lack of easy availability and handling problems are some of the difficulties associated with the use of calcium as a reducing agent. As against this, aluminothermic reduction of Nb_2O_5 based on the general reaction

$$Nb_2O_5 + (10/3+2y/x)\ Al = 2/x\ Nb_xAl_y + 5/3\ Al_2O_3$$

---

* E-Mail: juneja@magnum.barc.ernet.in

is best suited for the preparation of Nb-Al alloys. Here, aluminium acts both as a reductant as well as an alloying agent. Aluminium offers the following advantages over calcium: (1) it has low cost per chemical equivalent, (2) it is available in high purity and easy to handle and (3) the reduction with aluminium can be carried out in a thermite fashion in the open. The present paper describes aluminothermic reduction of Nb_2O_5 for the preparation of Nb-Al alloys of varying composition. The influence of various process parameters such as (i) the amount of aluminum in the charge, (ii) slag composition, (iii) requirement of heat energiser ($KClO_3$ + Al) etc. was studied to establish conditions for good slag-alloy separation and also to achieve optimum recoveries of the alloys.

PHYSICO-CHEMICAL ASPECTS OF ALUMINOTHERMIC REDUCTION OF Nb_2O_5

The reduction of Nb_2O_5 with stoichiometric amount of aluminium proceeds as per equation (1).

$$Nb_2O_5 + 10/3\ Al = 2Nb + 5/3\ Al_2O_3\,. \qquad (1)$$

Reaction (1) is feasible thermodynamically as indicated by the Gibbs energy data /14/ presented in Table 1. However, since niobium has a tendency to dissolve aluminium and form a number of intermediate phases (Nb_xAl_y), the aluminothermic reduction of Nb_2O_5 in the presence of excess aluminium proceeds via the general reaction

$$Nb_2O_5 + (10/3+2y/x)\ Al = 2/x\ Nb_xAl_y + 5/3\ Al_2O_3$$

The reactions involving formation of Nb_3 Al, Nb_2 Al and $NbAl_3$ intermediate phases are presented as reactions (2), (3) and (4) respectively in Table I. These reactions have more negative Gibbs energy changes as compared to that for reaction (1).

The specific heat for reaction (1), defined as the amount of heat released in kJ per kilogram of the reacting charge, is 2509 kJ/kg, which is sufficient for a thermite reaction. The specific heats for reactions (2) and (3) are also of the same order (> 2510 kJ/kg).

Table 1

Comparison of thermodynamic and physical parameters for aluminothermic reduction of Nb_2O_5 in the absence and presence of lime

Sl.No.	Reaction	$-\Delta G^0_{298K}$ (kJ)	$-\Delta H^o_{298K}$ (kJ)	Specific Heat of charge (kJ/kg)	Melting Point of phase (K)	
					Metallic	Slag
1.	$Nb_2O_5+10/3Al \rightarrow 2Nb+5/3Al_2O_3$	871.3	893.1	2509.3	2742	2323
2.	$Nb_2O_5+4Al \rightarrow 2/3Nb_3Al+5/3Al_2O_3$	911.9	944.6	2525.7	2333	2323
3.	$Nb_2O_5+13/3Al \rightarrow Nb_2Al+5/3Al_2O_3$	927.4	968	2527.7	2213	2323
4.	$Nb_2O_5+28/3Al \rightarrow 2NbAl_3+5/3Al_2O_3$	1037.9	1154.2	2228.5	1953	2323
5.	$Nb_2O_5+28/3Al+5/3CaO \rightarrow 2NbAl_3+5/3[CaO.Al_2O_3]$	-	-		1953	1873
6.	$KClO_3 + Al \rightarrow KCl + Al_2O_3$	-	1282.3	7274.7	-	2323

However, the specific heat for formation of aluminium-rich phase $NbAl_3$ [reaction (4)] is 2228 kJ/ kg, which is slightly less than the minimum required for a successful thermite reaction. Hence it may be necessary to incorporate thermal boosters ($KClO_3$ + Al) in the charge so as to provide sufficient heat for the reaction. The formation of $NbAl_3$ phase or other intermediate phases (Nb_2 Al and Nb_3 Al) in fact reduces the heat requirement for the reaction because of their lower melting points as compared to that for pure Nb metal (2742 K) [Table I]. The overall heat requirement for the slag-metal separation can be further reduced by forming lower melting slags for removing Al_2O_3 from the Nb-Al alloys. This was done by using lime based slags. Lime (CaO) combines with Al_2O_3 to form a slag containing calcium aluminate (CaO. Al_2O_3) which has a melting point of 1873 K as compared to the melting point of 2323 K for Al_2O_3.

THE THERMITE PROCESS

Several pure metals and many alloys are produced in large quantities by aluminothermic reduction, also known as the thermite process/ 15,16/. Such a process is generally a non-furnace process and uses the thermal energy, released during the reaction, to heat the metal/alloy and slag phases to the liquid state. The process is carried out under adiabatic conditions so as to conserve thermal energy inside the reactor and to retain the phases in liquid state so that sufficient time is available for slag-metal separation by density difference. During the stage of slag-metal separation (which may take a few minutes or more depending upon the total amount of the charge involved), a high temperature solvent extraction process takes place when the impurity elements present in the metal phase are extracted into the slag phase. This stage is similar to the one that takes place in iron-making in the blast furnace.

Aluminothermic reductions are generally performed in refractory lined reactors which may be either open type or closed bomb type. The reduction reaction is triggered either by local priming with an electric fuse or magnesium ribbon or by externally heating the reactor in a furnace. On completion of the reaction, the reactor is allowed to cool sufficiently, prior to separation of the reaction products. Simple physical or mechanical methods are generally applied for separation of the consolidated metal/alloy from slag.

EXPERIMENTAL

Niobium pentoxide (Nb_2O_5) used in the present investigation was of ~ 99.9 % purity and procured from the Nuclear Fuel Complex, Hyderabad. The oxide was calcined at 1073K prior to its use for thermite reduction. The aluminium powder (Grade C, - 120 mesh, purity > 98 %) used as the reductant was supplied by M/s Indian Aluminium Company. Lime (CaO), fluorspar (CaF_2) and potassium chlorate ($KClO_3$) were of technical grade and obtained from local suppliers.

The reduction was carried out in clay bonded graphite or mild steel reactor (0.20 m dia x 0.75 m high x 0.003 m thick plate) lined with calcined magnesia to a thickness of 0.05 m on the sides and 0.075 m at the bottom. The experiments were carried out in batches of a charge containing 100 g Nb_2O_5. The reactants consisting of Nb_2O_5, Al, CaO, CaF_2 and $KClO_3$ were mixed intimately in the required proportions and charged into the lined reactor. A trigger mixture of $KClO_3$+Al (1:1) was placed on the top surface of the charge. The reaction was initiated by igniting the trigger mixture with a burning magnesium ribbon. The reaction proceeded briskly to completion and the alloy was recovered from the reacted mass after it was allowed to cool for a sufficient time.

RESULTS AND DISCUSSION

The preparation of Nb-Al alloys corresponding to Nb-Al solid solution, Nb_3Al, Nb_2Al, and $NbAl_3$ phases was studied by a liquid-liquid slag-metal separation using the thermite process. Fluxes like CaO and CaF_2 were added to the thermite charge to decrease the melting point of the slag and to increase the fluidity of the slag. Results of these studies are presented in Table 2.

The Nb-Al solid solution alloys were obtained when Nb_2O_5 was reduced with Al according to reaction (1) given above. A maximum yield of 71.4 % of niobium thermite metal was obtained when reduction was carried

Table 2

Results of aluminothermic reduction of Nb_2O_5 on 100 g Nb_2O_5 scale.

Product	Sl. No.	Charge Composition(g)				Al Excess over stoichiometry (%)	Yield (%)	Remarks
		Al	$KClO_3$	CaO	CaF_2			
Nb-Al s.s.	1.	34.0	-	-		0	71.4	Good slag-metal separation
	2.	36.2	5	17	5	0	72.0	Very good slag metal separation
	3.	37.7	5	17	5	5	77.7	,,
	4.	39.4	5	17	5	10	84.3	,,
Nb_3Al	5.	40.6	-	-	-	0	58.7	Good slag-metal separation
	6.	42.8	5	17	5	0	77.0	Very good slag metal separation
	7.	44.8	5	17	5	5	83.0	,,
	8.	46.9	5	17	5	10	88.9	,,
Nb_2Al	9.	44.0	-	-	-	0	72.5	Good slag-metal separation
	10.	46.2	5	17	5	0	79.6	Very good slag metal separation
	11.	48.4	5	17	5	5	85.0	,,
	12.	50.6	5	17	5	10	86.0	,,
$NbAl_3$	13.	95.0	0	-	-	0	-	No slag-metal separation
	14.	99.4	10	-	-	0	-	Slag entrapped in alloy
	15.	101.4	15	-	-	0	78.7	Good slag-metal separation
	16.	101.4	15	19	6	0	85.6	Very good slag metal separation
	17.	107.0	15	19	6	5	93.3	,,
	18.	112.0	15	19	6	10	97.8	,,

s.s.: solid solution

out with stoichiometric amount of aluminium. Addition of 17 g CaO and 5 g CaF_2 along with 5 g $KClO_3$ to the charge was found to give still better slag-metal separation because of formation of lower melting slag. The alloy recovery using these fluxes was, however, 72 %. The use of 17 g CaO, 5 g CaF_2 and 5 g $KClO_3$ were the minimum quantities required for achieving good slag-metal separation. Further increase in the quantities of these fluxing agents in the charge was not found to be beneficial. Variation of the amount of aluminium in the charge from 0 to 10 % excess over stoichiometric requirement resulted in improving the alloy yield from 72 % to 84.3 %. However as reported in literature, it is possible to obtain Nb-Al s.s. alloys with still higher recovery by using higher excess of Al in the charge /17/. The thermite metal obtained with 5 % excess Al was found to analyse as 92.3 % Nb, 4.5 % Al, 0.084 % oxygen and 0.004 % nitrogen.

Alloys corresponding to Nb_3 Al phase composition were prepared based on reaction (2)

$$Nb_2O_5 + 4\,Al = 2/3\,Nb_3Al + 5/3\,Al_2O_3 \qquad (2)$$

Table 2 also presents the results of these studies. Reduction of Nb_2O_5 with stoichiometric amount of aluminium resulted in an alloy yield of 58.7 % without addition of any fluxing agents and an alloy yield of 77 % with the use of 5 g $KClO_3$, 17 g CaO and 5 g CaF_2 per 100 g Nb_2O_5. Studies on the variation of excess Al in the charge showed that the yield of the alloy could be improved from 77 to 88.9 % as the % excess Al was increased from 0 to 10 %. The alloy obtained with 5 % excess Al was found to contain 91.2 % Nb, 7.6 % Al, 0.054 % oxygen and 0.03 % nitrogen.

Preparation of alloys corresponding to Nb_2 Al phase composition was as per reaction (3)

$$Nb_2O_5 + 13/3\,Al = Nb_2Al + 5/3\,Al_2O_3. \qquad (3)$$

The results of these studies are also presented in Table 2. As is evident from the data in Table 2, a maximum alloy yield of 72.5 % was obtained when Nb_2O_5 was reduced with stoichiometric amount of aluminium. The alloy yield could be improved to 79.6 % when the reduction was carried out in presence of 5 g $KClO_3$, 17 g CaO and 5 g CaF_2 per 100 g Nb_2O_5. Addition of 5 & 10 % excess aluminium over the stoichiometric requirement helped to increase the alloy yield to 85 & 86 % respectively. The alloy obtained with 5 % excess Al was found to analyse 82.3 % Nb, 17.5 % Al, 0.0343 % oxygen and 0.0045 % nitrogen.

The alloys corresponding to $NbAl_3$ phase composition were obtained as per reaction (4)

$$Nb_2O_5 + 28/3\,Al = 2NbAl_3 + 5/3\,Al_2O_3 \qquad 4)$$

As is evident from the data in Table 2, the reduction of Nb_2O_5 with stoichiometric amount of Al did not yield any slag-metal separation. This was because the specific heat of the charge is low (2228.5 kJ/kg) and is not adequate for good slag-metal separation. Addition of $KClO_3$ as heat booster to the extent of 15 g per 100 g Nb_2O_5 was found to be necessary to get good slag-metal separation. Such a charge gave an alloy yield of 78.7 %. The alloy yield could be further improved to 85.6 % by incorporating in the charge fluxing agents CaO and CaF_2 to the extent of 19 g and 6 g respectively per 100 g Nb_2O_5. Increasing the amount of CaO beyond 19 g per 100 g Nb_2O_5, however, resulted in decreasing the alloy yield. It may be noted here that use of minimum quantities of CaO and CaF_2 is desirable as otherwise the heat balance of the charge is offset. Studies on the variation of the excess of Al in the charge indicated that the alloy yield improved from 85.6 to 97.8 % as the excess of Al over stoichiometric requirement was varied from 0 to 10 %. An alloy obtained from a charge containing 5 % excess Al was found to analyse 54.6 % Nb, 45.2 % Al, 0.516 % oxygen and 0.009 % nitrogen.

Table 3 presents the % extraction of Nb calculated for different alloys obtained with 5 % excess Al in the charge. The excess of Al in the charge was fixed at 5 % so as to get alloys close to the stoichiometric compositions. Whereas the $NbAl_3$ alloys have been obtained with a high Nb extraction of 95. 3 %, the corresponding value for Nb-Al s.s. is 71.8 %. The % extraction of Nb obtained for $NbAl_3$, Nb_2Al and Nb_3Al alloys is quite good, being > 80 %. The composition of these alloys is also near to the theoretical value. Their composition can be further adjusted during the final melting stage. The % extraction of Nb for Nb-Al s.s. can be further improved by using higher excess of Al in the charge. However, in that case the alloys may not

Table 3

Results showing alloy yield, composition and extraction coefficient of Nb for various alloys obtained from charges containing different Al/Nb_2O_5 ratios (with 5 % excess Al over stoichiometric requirement).

Product	Theor. Nb (%)	Al/Nb_2O_5 Molar ratio	Alloy Yield (%)	Alloy composition			Nb Extraction (%)
				Nb(%)	O(%)	N(%)	
$NbAl_3$	53.45	9.33	93.3	54.6	0.516	0.009	95.3
Nb_2Al	87.32	4.33	85	82.3	0.0343	0.004	80.3
Nb_3Al	91.18	4.00	83	91.2	0.054	0.030	83.1
Nb-Al s.s.	96.77	3.33	77.7	92.3	0.084	0.004	71.8

s.s.: solid solution

conform to the near stoichiometric composition as desired in the present investigation. The oxygen and nitrogen contents of different alloys (Table 3) are quite low.

CONCLUSIONS

The Nb-Al alloys containing 54 to 92 % Nb can be prepared by open aluminothermic reduction of Nb_2O_5 using different amounts of aluminium. The alloys obtained have quite low values of oxygen and nitrogen contents.

REFERENCES

1. P.R Subramanian., M.G. Mendiratta and D.M. Dimiduk, *J.Metals*, 33 (January, 1996).
2. J.J. Stephans, *J. Metals*, **42** (8), 22 (1990).
3. M.G. Hebsur, *Intermetallics*, **2,** 43 (1994).
4. C. Laverik, *J. Less-Common Met.*, **139,** 107 (1988).
5. R. Akihama, R.J. Murphy and S. Foner, *IEEE Trans. Magn., MAG*, **17,** 274 (1981).
6. H.A. Lipsitt, *High Temp. Ordered Interm. Alloys*, C.C. Koch, C.T. Liu and N.S. Stoloff (Eds.), MRS Proc., **39,** 35 (1985).
7. E.A.Loria, *Proc. Int. Symp. on Ta & Nb*, Orlando, Florida, USA, Tantalum-Niobium International Study Centre , Belgium (1988) p.631.
8. C.K. Gupta and A.K. Suri, *Extractive Metallurgy of Niobium in Purification and Consolidation*, CRC, Boca Raton, (1993) p.212.
9. K. K. Schulze , *J. Met.* **33** (5), 33 (1981).
10. T.B. Massalski, *Binary Alloy Phase Diagrams*, ASM International, Materials Park, OH, (1990).
11. G.Li X., A.Chiba, K. Ohsaki, Y. Morita and M. Uda, *J. Alloys & Compounds*, **238**, 202(1996).
12. J.C. Murray and R.M. German, *Met. Trans.* **23 A,** 2357 (1992).
13. T.H. Okabe, K. Fujiwara, L.T. Oishi and K.Ono , *Met. Trans.* **23 B,** 415 (1992).
14. NIST-JANAF Thermochemical Tables, 4th Edition, *J. Phys. Chem. Ref. Data, Monograph 9*, Amer. Chem.Soc. & the Amer. Inst. of Phys., New York (1998).
15. D. Belitskus, *J. Metals*, 3, (January 1972).
16. F.H. Perfect, *Trans. Metal. Soc. of AIME*, **239**, 1282 (1967).
17. G.R. Kamat and C.K. Gupta , *Met. Trans.*, **2**, 2817 (1971).