THE PRODUCTION OF NIOBIUM-BEARING FERRO-ALLOYS IN THE USSR

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Summary

Various types of niobium-containing raw materials used in the production melting of alloys which utilize niobium additions are discussed. The details of the production of such alloys are presented. The composition of concentrate, of the technically available forms of niobium and of various types of ferroniobium and niobium alloys is reported. Methods used to facilitate increased extraction of niobium and the elimination of residual elements are described.

The Production of Niobium-Bearing Ferro-Alloys

At the present time, niobium is finding increasing use as an alloying element in the production of high-quality special-purpose steels and alloys. In addition to expanding usage in traditional grades of steels such as stainless and heat-resistant, the use of niobium is increasing in ordinary structural grades of steel used in a variety of applications.

The main kinds of niobium-bearing raw materials used for smelting niobium alloys are commercial niobium pentoxide and niobium concentrate produced by beneficiation of pyrochlore ores. The chemical composition of concentrates produced varies within the following ranges shown in Table I below (in weight percent).

Table I. Chemical Composition of Pyrochlore Concentrate

$Nb_2O_5 + Ta_2O_5$	38 - 43%
SiO_2	11 - 14%
TiO_2	7 - 14%
C	0.03 - 0.10%

The ratio of niobium to tantalum in the concentrate is 40:50. Pyrochlore concentrates produced in other countries (Brasil, Canada, and Nigeria) usually have higher contents of niobium and lower contents of impurities such as silicon, titanium, phosphorus and the like. As an example, the chemical composition of the concentrate produced from the Araxa deposit in Brasil contains: -- 60.9 percent Nb_2O_5; 0.14 percent SiO_2; and 4.0 percent TiO_2. (See paper by Paraiso and DeFuccio in this volume.)

For smelting niobium alloys, commercial niobium pentoxide with the following composition is used shown in Table II below (weight percent).

Table II. Chemical Composition of Commercial Niobium Pentoxide

Nb_2O_5	SiO_2	P	C	S
87 - 99.5	0.2 - 1.8	0.05 - 0.40	0.03 - 0.10	0.01 - 0.20

Both ferroniobium and niobium-bearing alloys are made by the aluminothermic process.

Until recently, ferroniobium was smelted only by the off-furnace aluminothermic process in a stationary vessel utilizing top ignition, all of the prepared charge being fed into the melting vessel prior to ignition. The introduction of bottom-ignition smelting has resulted in a sharp rise in the technical and economical parameters relating to ferroniobium production.

Maximum niobium recovery during smelting is attained at a niobium content in the alloy of 60 - 70 percent, this requires addition into the charge of 30 - 40 percent iron ore, along with the commercial niobium pentoxide, thus resulting in the production of an alloy which is close to the eutectic composition in the Fe-Nb system.

The influence of the quantity of iron ore in the smelting charge on niobium recovery in the ingot (1) and on the niobium content in the alloy (2) is shown in Figure 1. The influence of the reductant quantity in the charge on niobium recovery and aluminum content in the alloy is shown in Figure 2. The data show that increasing the quantity of aluminum in the charge above certain limits (109 - 111 percent of that calculated from stoichiometry) results in a reduction in niobium recovery since the increase in aluminum content decreases alloy density and consequently produces less favorable conditions for metal ingot formation. For off-furnace smelting, the quantity of lime in the charges influences niobium recovery as shown in Figure 3, with the optimum quantity equal to 30 percent of the mass of niobium pentoxide.

When carrying out off-furnace ferroniobium melting involving melt tapping, it is advisable to limit the quantity of lime added to the charge using partial substitution with powdered magnesite; thereby decreasing the slag viscosity. The viscosity reduction apparently results from the formation of less stable complex anions, which decompose at 1600 - 1700 C to produce simpler ones with lower viscous-flow activation energies (2).

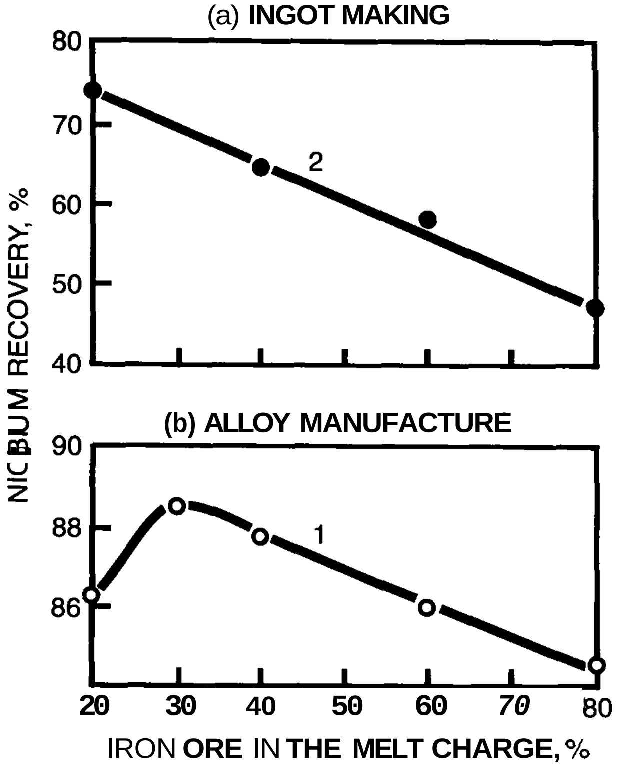

Figure 1. Influence of the amount of iron ore in the charge on (1) niobium recovery in ingots and (2) niobium content in the alloy in ferroniobium smelting.

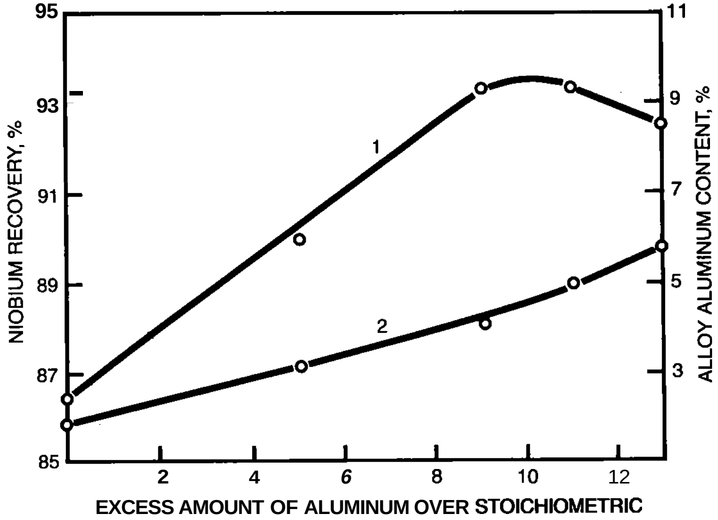

Figure 2. Influence of the amount of reductant in the charge on (1) niobium recovery and (2) aluminum content in the alloy.

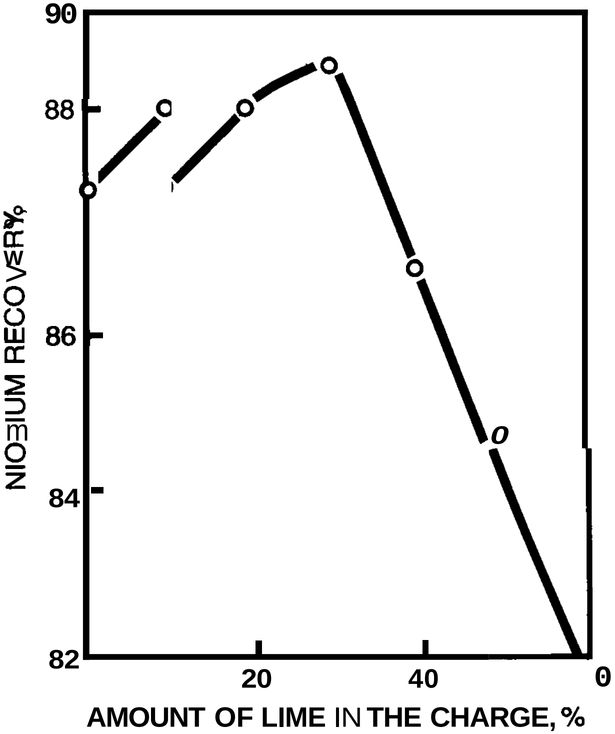

Figure 3. Influence of the amount of lime in the charge on niobium recovery.

Ferroniobium is smelted on an industrial scale from commercial niobium pentoxide in a tilting melting vessel. Melting is carried out with bottom ignition at a charge melting rate of 160 - 180 kg/m^2. min., to yield a recovery of 94.5 percent. The specific heat of the process is 85.4 kJ/gr-atom of charge, or when relating the heat released to each gr–atom of metal, it amounts to 424 kJ. In comparison with oxide raw materials, smelting ferroniobium from pyrochlore concentrate requires at least 900 kJ per gr–atom of metal.

Electric furnace smelting of ferroniobium from pyrochlore concentrates is carried out in a magnesite–lined steel melting furnace, type DC-3 at a voltage of 140V. The roof and arch of the charging door are lined with chrome–magnesite bricks and the finished melt is poured into a mould lined with magnesite bricks.

In the industrial electric furnace smelting of ferroniobium from pyrochlore concentrates aluminum powder is used as a reductant; in addition, iron ore (95 - 97% Fe_2O_3) is added for improving the energy conditions of the process and to produce an alloy with the required composition. In certain cases, part of the iron ore may be replaced by metallic iron. All charge materials are used in powdered form with a particle size of less than 2 mm, and are carefully blended before melting. Materials consumption per ton of metal containing 50 percent total niobium and tantalum is: 2425 kg of niobium concentrate (30% $Nb_2O_5 + Ta_2O_5$); 585 kg primary aluminum powder and 145 kg of upgraded iron ore. Power consumption per ton of alloy is 2000 kWh, and niobium recovery in smelting is 97 - 98.5 percent. In comparison with the off–furnace smelting process aluminum consumption is reduced by 30 percent and impurity contents are decreased as follows: titanium by 1.5 times, aluminum by 2.7 times, sulphur by 3.2 times and nitrogen by 5 times. There is almost no segregation in the ferroniobium ingot which distinguishes the process from off–furnace and two–stage methods of ferroniobium block smelting.

In the Soviet Union, five grades of ferroniobium are produced containing, in general, 50 - 70 percent niobium.

Contents of accompanying elements such as cobalt, tin, lead, zinc, arsenic, bismuth and nitrogen are determined, but reporting is not specified by the standard.

Ferroniobium Grades FNO, FNI and FN2 are smelted from commercial niobium pentoxide in a tilting melting hearth furnace using melt tapping and bottom ignition. Recovery of niobium is 94.5 percent and metal is poured into unlined cast–iron moulds.

Typical chemical compositions of alloys FND, FNI and FNZ are shown in Table III below (weight percent).

Table III. Chemical Composition of Commercial Ferro Niobium Alloys, FND, FNI, FN2

Nb + Ta	Si	Al	Ti	C	S	P
60–62	0.8-1.7	1.1–4.2	< 0.1	0.04–0.09	0.01-0.02	0.06–0.14

The content of non–ferrous metal impurities is: 0.0015 percent Pb, 0.005 percent Co, Zn, Sb, Bi and Sn, and less than 0.01 percent As.

Ferroniobium grades FN3 and FN4 are produced from pyrochlore concentrate by electric arc furnace smelting. Prior to melting, the lining is heated by melting metallic scrap and lime-magnesium slag is produced. After heating, the slag is thinned with fluorspar and the melt is poured into a slag pot, thereafter the charge is fed from the furnace bin into the heated furnace to commence ferroniobium smelting. Melting utilizes 1700 kg concentrate and a voltage of 140 V with the melt being poured into a cast-iron mould. About 1100-1200 kg of metal are produced from each charge. Power consumption per ton of alloy is 200 kWh and niobium recovery is about 98.5 percent.

Following, Table IV, are typical chemical compositions of the alloy (weight percent).

Table IV. Chemical Composition of Commercial Ferro Niobium Alloys, FN3, FN4

Grade	Nb+Ta	si	Al	Ti	C	S	P
FN3	53-62	11.2-13.0	0.5-3.4	2.2-6.7	0.1-0.2	0.01	0.06-0.10
FN4	53-58	11.5-13.0	0.5-3.4	3.5-8.0	0.15-0.24	0.01	0.17-0.43

The niobium-iron system is most important for investigating the relevant conditions for the use of niobium in the ferrous metallurgy. The constitutional diagram shows that the liquidus temperature of Nb-Fe binary alloys in the niobium concentration range of 60 - 65 percent does not exceed 1670 C. Furthermore, it should be noted that even in the concentration range of 50 - 60 percent niobium, the liquidus temperature of Nb-Fe alloys exceeds the optimum temperature for steel alloying. This is well shown in Table V below, which contains the results of ferroniobium melting temperatures measured by contact method in a unit made in the Central Scientific Research Institute for Ferrous Metallurgy (CNIICHERMET).

Table V. Alloy Melting Temperatures

Composition, wt %		
Nb	Fe	Arithmetic Mean Temperature, C
40	60	1658
50'	50	1676
60	40	1613

In addition to the above grades of ferroniobium, a number of special niobium-bearing alloys are made containing nickel, chromium, manganese and aluminum depending on consumer preference.

For example, nickel-niobium master alloys are made in electric furnaces using commercial niobium pentoxide and electrolytic nickel. Two grades are produced having the chemical compositions shown in Table VI below.

Table VI. Chemical Composition of the Nb-Ni Master Alloys (wt %)

Grade	Nb	Al	Si	Fe	C	Ni
NNb-1	30-45	<3.0	<1.0	<1.2	<0.1	Balance
NNb-2	30-45	<5.0	<1.0	<1.5	<0.1	Balance

Niobium recovery is 90 percent and power consumption per ton of alloy is 700 to 800 kWh. The melting temperature of nickel-niobium master alloys (50 to 60% Nb) are lower than those of ferroniobium (40 to 60% Nb) by about 350 to 450 C.

Chromium-niobium master alloys are also made by the off-furnace process from niobium pentoxide, chromium oxide, calcium chromate and aluminum powder in the ratio of 1:0; 4:0; 2:0,6.0 respectively. The chemical compositions of the master alloys are given in Table VII below.

Table VII. Chemical Compositions of Nb-Cr Master Alloys (wt %)

~~Grade~~	Nb	Fe	Al	Si	Ti	P	C	S	Cr
HNB	55-65	<2.0	<2.0	<1.0	<1.0	<0.1	<0.05	<0.02	Balance
HNbx	55-65	<15.0	<2.5	<1.5	<1.0	<0.15	<0.10	<0.02	Balance

Chromium - iron - niobium master alloy (HNbx) is made in an electric arc furnace by premelting a blend of chromium concentrate (60% Cr_2O_3, 1% SiO_2, 13% FeO) and lime followed by subsequent loading onto the molten surface the part of the charge to be reduced. The charge comprises niobium pentoxide, aluminum powder and chromium concentrate. For both alloys niobium recovery is in the range to 92 - 96 percent, and chromium recovery is 90 - 95 percent.

Binary chromium-niobium master alloy can also be made in electric arc furnaces by aluminothermic reduction of pyrochlore concentrate and chromium oxide mixtures. The resulting aluminum content in the alloy produced can be reduced if desired by oxygen blowing into the furnace.

For production of C-Mn-Nb steels, it is feasible to use niobium-manganese master alloys which have lower melting temperature than ferroniobium and, which thus quickly dissolve in the steel. The manganese-niobium master alloy is made using the off-furnace aluminothermic process by combined reduction of pyrochlore-concentrate, oxides and manganese ore (79% MnO_2). The alloy produced is constituted as follows in Table VIII.

Table VIII. Composition of Low Melting Point Fe-Mn-Nb Alloys (wt %)

Nb	Mn	Si	Al	Ti	Fe
30 - 45	19 - 29	6 - 8	3 - 5	4 - 5	Balance

The phosphorus content in the alloy made from manganese ore is 0.38 percent, while when using metallic manganese it does not exceed 0.11 percent. The melting temperatures of dilute niobium-manganese-iron master alloys containing up to 5 percent manganese do not differ significantly from that of ferroniobium (50% Nb). However, once the manganese content is increased to 30 percent, the melting temperature is lowered by 120 C.

Aluminum-niobium master alloys may also be made in the electric arc furnace by premelting of secondary aluminum pigs and subsequent addition into the melt surface of a charge consisting of pyrochlore concentrate, iron ore, secondary aluminum powder (90% Al, 5% Si, 4% Cu) and lime. The chemical composition of the resulting master alloy is as follows in Table IX.

Table IX. Chemical Composition of Nb-Al Master Alloys

Nb	Al	Si	Ti	P	Cu	Fe
17 - 25	28 - 40	8 - 10	5 - 7	0.10 - 0.15	3 - 5	Balance

The waste slags generated by the niobium alloys industry are a very valuable raw material for the production of alumina, refractories, cement, and the like, and are widely used in the Soviet Union for these purposes.

Conclusion

The achievement of superior economic and technical parameters in the production and use of niobium-bearing master alloys is possible only when the method of master alloy production is rationally chosen. Consideration of the influence of the main production factors on the niobium recovery and careful study of the metallurgical properties of master alloys is most important. Abundant experience has been accumulated regarding the use of various types of niobium-bearing raw materials for the production of niobium-bearing master alloys.

References

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