

Technology of Niobium Ferroalloys

Mihail I. Gasik

National Metallurgical Academy of Ukraine, Dnipropetrovsk, Ukraine

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14.1 PROPERTIES OF NIOBIUM

Niobium (an American term also referred to as columbium, Cb) belongs to the group V elements of the periodic table. It has number 41, an atomic weight of 92.9, a density of 8.57 g/cm³, and an atomic electron configuration of 4d⁴5s¹. The most stable compounds are formed with pentavalent niobium (+5), but there are also known compounds with oxidation states +4, +3, +2, and +1. The melting temperature of niobium is reported to be 2470°C, and the boiling point is 4927°C. The crystal lattice of niobium is body-centered cubic (BCC) with a = 0.3294 nm.

Niobium has become useful in steelmaking because of its ability to control carbides, nitrides, and material grain size, especially at elevated temperatures. Niobium in steels forms finely dispersed carbide NbC and nitride NbN. Niobium improves the resistance of stainless steels to intercrystallite corrosion, reaching its maximal value at mass ratios Nb/C > 10. Niobium alloyed (<1.5% Nb) chromium–molybdenum steels (2% to 13% Cr, <0.6% Mo) are often used in high-temperature applications such as for boilers. In low-alloyed steels, niobium is widely used as a microalloying element, which in combination with

controlled thermal-mechanical treatment is important for many varieties of high-strength, low-alloy (HSLA) steels. Minor niobium additions also promote the corrosion resistance of iron alloys. As a metal, niobium has applications in tool steels, wear- and abrasion-resistant and stainless steels, and various superalloys (Eggert et al., 1982).

Niobium and iron have complete mutual solubility in the liquid state (Fig. 14.1). In the solid state, several intermetallic compounds form, such as $\text{Nb}_{19}\text{Fe}_{21}$ (also reported as Nb_6Fe_7 ; decomposition $> 1500^\circ\text{C}$) and NbFe_2 (1655°C). The existence of η -phase Nb_3Fe_2 has also been mentioned. Alloys such as standard ferroniobium ($\sim 50\%$ to 70% Nb + Ta) have liquidus points in the range 1580° to 1620°C .

With carbon niobium forms two stable carbides (Fig. 14.2): Nb_2C (5.43% to 5.83% wt. C) and NbC (stoichiometric compositions 11.45% wt. C, melting point 3613°C , density of 7.82 g/cm^3). Carbides have a wide range of homogeneity. The existence of metastable carbide Nb_3C_2 has not yet been confirmed. Carbide Nb_2C has three modifications: α -phase (rhombohedral $< 1200^\circ$ to 1230°C), β -phase (hexagonal, 1200° to 2500°C), and γ -phase (disordered hexagonal, $> 2500^\circ\text{C}$). Maximal solubility of carbon in solid niobium is up to 1% wt. C at eutectic temperature.

Niobium has a high affinity for phosphorus, forming the thermodynamically strong phosphides NbP (with a wide homogeneity range $\text{NbP}_{0.8-1.2}$) and NbP_2 . The latter phosphide decomposes upon melting ($\sim 1730^\circ\text{C}$).

In the system Nb-Si (Fig. 14.3), three stable silicides have been identified: Nb_3Si , Nb_5Si_3 , and NbSi_2 , among which Nb_5Si_3 has different structures in high-temperature (β) and low-temperature (α) ranges. This intermetallide usually

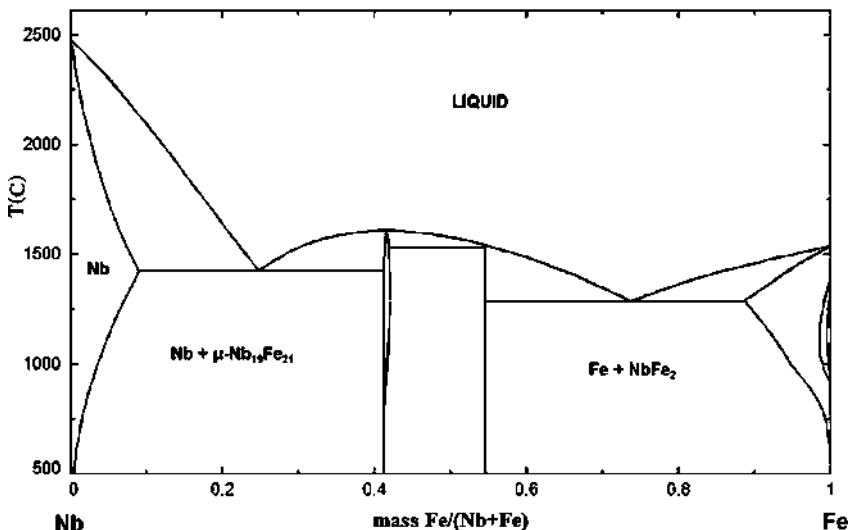


FIGURE 14.1 Equilibrium state diagram of the system Nb-Fe.

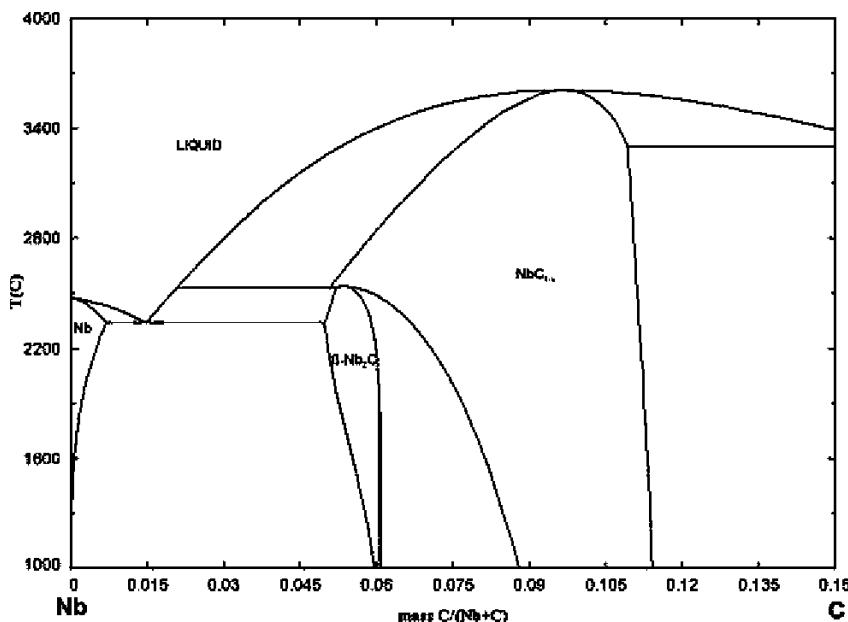


FIGURE 14.2 Equilibrium diagram of the system Nb-C.

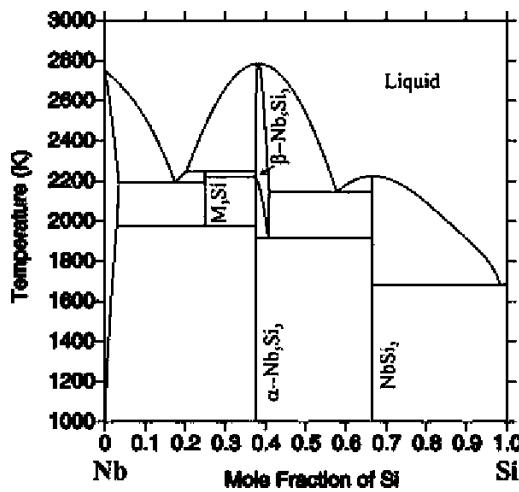


FIGURE 14.3 Equilibrium diagram of the system Nb-Si.

forms in the standard FeNb alloy and increases the melting temperature of the alloy. Silicon dissolves in Nb < 0.5 at. % at 1170°C and < 1.2 at. % at 1920°C, but niobium is practically insoluble in silicon. The silicon percentage in FeNb actually determines its liquidus temperature, phase constitution, and density.

With aluminum niobium forms a number of niobium aluminides—NbAl₃, Nb₂Al, and Nb₃Al (Fig. 14.4)—all having rather high melting points: 1694, 1933, and \sim 2050°C, respectively. The eutectic temperature in the NbAl₃–Nb₂Al range is 1598°C. The solubility of Al in niobium at peritectic temperature is 21% to 23% at. Al, and niobium in aluminum is below 0.3% at. Nb.

With oxygen, niobium forms three stable oxides (Fig. 14.5), namely NbO (melting point 1945°C), NbO₂ (melting point 1915°C), and Nb₂O₅ (melting point 1510°C). The latter oxide is a commonly appearing form in niobium-containing minerals and is a base for many niobate systems. It has three known modifications, of which the monoclinic β -phase is the most stable for metallurgical conditions. The other two phases eventually appear during the oxidation of niobium at low (α -phase) or high (γ -phase) temperatures.

Another oxide phase, Nb₄O₅ (not shown in Fig. 14.5; tetragonal lattice type), was found in the residuals of electrolysis of Nb-O-F melts, and its formation mechanism has not yet been studied.

Three niobates are formed with calcium oxide (Fig. 14.6) as CaO·Nb₂O₅, 2CaO·Nb₂O₅, and 3CaO·Nb₂O₅, all of them with rather high melting points.

Contrary to CaO, there are no chemical compounds in the Nb₂O₅–SiO₂ system, which is of a eutectic type. Both oxides Nb₂O₅ and SiO₂ have an acidic nature. Above 1695°C there is a wide region of two immiscible liquids. With alumina, Nb₂O₅ does form three stable compounds: Al₂O₃·Nb₂O₅, Al₂O₃·9Nb₂O₅, and Al₂O₃·25Nb₂O₅.

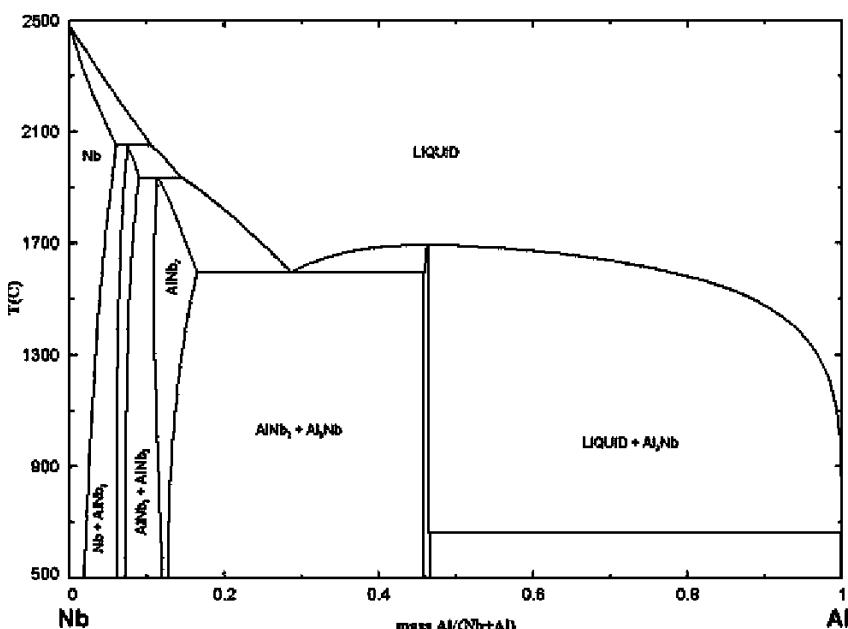


FIGURE 14.4 Equilibrium state diagram of the system Nb-Al.

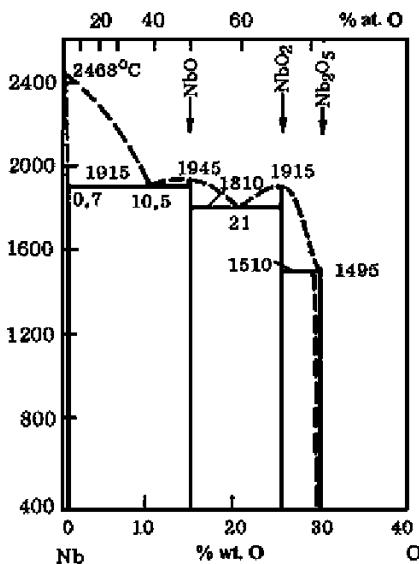


FIGURE 14.5 Phase diagram of the system Nb-O.

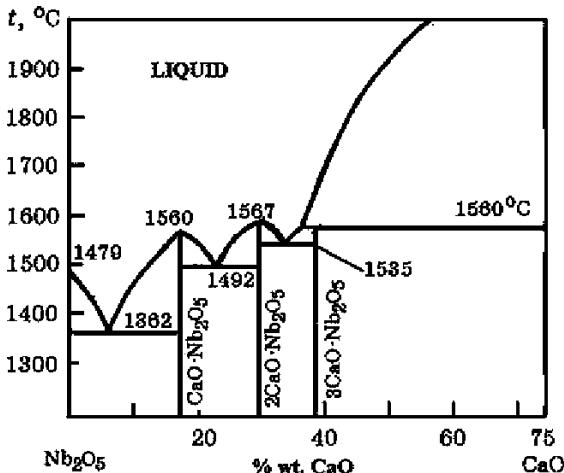


FIGURE 14.6 Equilibrium state diagram of the system Nb₂O₅-CaO.

14.2 SOURCES OF NIOBIUM AND ITS REDUCTION

14.2.1 Minerals of Niobium

Niobium, together with tantalum, appears in a large group of minerals (tantalum-niobates). A generalized formula of these minerals might be written as $A_nB_mX_p$, where “A” represents cations of large size (Ca^{2+} , REM^{3+} , U^{4+} ,

Th⁴⁺, Na⁺, and possibly Pb²⁺, Sb²⁺, Bi³⁺) and medium size (Fe²⁺, Mn²⁺, Mg²⁺); “B” sites are Nb⁵⁺, Ta⁵⁺, replacing Ti⁴⁺, Sn⁴⁺, Fe³⁺; and anions “X” are O²⁻, OH⁻, F⁻. Of the more than 130 known minerals that contain niobium (tantalum), six minerals are of a direct industrial relevance (Gasik et al., 2009). The most important niobium minerals that compose the niobium ores are columbite (Fe,Mn)(Nb,Ta)O₆ (~50% to 67% Nb₂O₅) and pyrochlore (Ca,N-a)₂(Nb,Ta,Ti)O₆(OH,F) with ~40% to 70% Nb₂O₅. If tantalum is dominating in columbite instead of niobium, the mineral is called tantalite. In some deposits, equally important is loparite (Ca,Na,Ce)(Ti,Nb,Ta)O₃ (~7–20% Nb₂O₅). It falls in the class of niobium and rare earth perovskites (CaTiO₃), where calcium is partially replaced by REM, and titanium by niobium and tantalum. Besides loparite, other similar minerals of this type are knopite (CeTiO₃) and dizanalite (Ca,Na,Ce)(Ti,Nb,Fe)O₃.

Industrially suitable niobium ore, from which it is cost-effective to obtain niobium concentrates, contains at least 0.15% to 0.20% wt. Nb₂O₅. In the richest niobium ores known in the world, the Nb₂O₅ content may reach up to 1% to 4%. The leading mineral resources of niobium at the moment are in Brazil (84.2% of total), Canada (9.8%), and Zaire (4.2%). The primary Brazilian ore is the pyrochlore type, which is easier to enrich than the columbite/tantalite ores (Gupta et al., 1994).

14.2.2 Reduction of Niobium

A reduction reaction of Nb₂O₅ by carbon is possible, but it will ultimately lead to the formation of niobium carbide (NbC). This practically excludes carbon from potential reductant lists, as niobium ferroalloys are limited in carbon content because of their intended applications.

Practically, niobium might be reduced either by silicon or aluminum. With silicon, the reaction Nb₂O₅ + Si = Nb + SiO₂ does not proceed to a great extent, and the extraction degree of niobium in such a process is usually small. The alloy with 50% to 60% Nb in this case is obtained with a high content of silicon (5% to 8% Si).

The best extraction of niobium is achieved via the reduction by aluminum, which has favorable thermodynamics for the reaction between Nb₂O₅ and aluminum 3Nb₂O₅ + 10Al = 6Nb + 5Al₂O₃ (~1000 kJ/mol oxide Nb₂O₅) but less favorable for the reaction 3NbO + 2Al = 3Nb + Al₂O₃ (~165 kJ/mol oxide NbO). The temperatures of the aluminothermic process reach 1800° to 2000°C and the extraction of niobium into the alloy approaches 99.8%.

14.3 TECHNOLOGY OF NIOBIUM FERROALLOYS

The content of niobium in standard ferroniobium is normally from 55% to 65% wt. The alloy also contains <2 Si, <5 Al, <2 Ti, <0.3 C, <0.03 S, <0.05 to 0.10 P, balance – Fe. The highest premium grades with 62% to 70% wt. Nb +

Ta are additionally limited in aluminum (<1% Al) and other components content (<0.2 Si, <0.1 C, 0.3 Ta, <0.5 Mn, <0.5 Cr, <0.02 S, <0.02 P). Because the concentration of niobium in most low-alloy and HSLA steels is less than 0.1% and in the highly alloyed steels <~1%, such impurities in the niobium ferroalloys do not usually present a problem, with the possible exception of phosphorus. On the other hand, as shown later, lower-grade FeNb alloys (50% to 60% Nb) with higher silicon (<15%) might also be produced from specific ores. However, this FeSiNb grade is more difficult to dissolve in steels than FeNb with low silicon, and thus the alloy is first crushed down to sizes below 20 mm. Most FeNb lumps might have relatively high gas concentrations (<0.05% to 0.2% wt. N, <0.2 O, <0.01 H). To improve the addition of niobium to steels, Nb-lean alloys and different master alloys have been designed and produced, among which Fe-25Nb, Fe-25Mn-40Nb, and Fe-30Ti-16Nb-10Al compositions could be mentioned (Gasik et al., 2009).

All smelting processes use niobium pentoxide Nb_2O_5 and niobium concentrates. The pentoxide should have more than 95% Nb_2O_5 and a limited amount of other impurities. The range of the variation of impurities (depending on the source) is (% wt.) 0.1 to 1.2 Ta_2O_5 , 0.02 to 1.8 SiO_2 , 0.06 to 0.9 TiO_2 , 0.09 to 4 Fe_2O_3 , 0.05 to 0.4 P, 0.03 to 0.1 C, 0.01 to 0.2 S, <0.02 As, <0.0006 Pb, and <0.03 Sn.

The methods for ferroniobium processing by aluminum reduction include (1) off-furnace smelting “on the block” (ingot), (2) smelting in the ladle with the release of metal and slag, and (3) smelting in an electric arc furnace.

The first method is no longer widely used because it has certain drawbacks, among which are the nonoptimal combination of smelting and crystallization of the metal and slag in one unit, the increased amounts of the charge and refractory materials required, higher labor costs for lining and disassembly of the reactor furnaces, and cleaning of metal and refractory slag. A single use of a reactor and the necessity to move each furnace with the liquid products from the melting chamber to the site for cooling add to the complexity of the process.

The second method includes the release of ferroalloy slag. In exothermic reactions, heat release is sufficient to self-sustain the process. The charge for this method consists of 100 kg of niobium pentoxide, 52 to 60 kg of aluminum, 38 to 40 kg of iron ore pellets, 20 kg of iron scale, 30 kg of lime, and ~0.1 kg of sodium nitrate (NaNO_3) to initiate the reaction. The melting rate after initiation of the reaction proceeds with rates of 160 to 180 $\text{kg}/(\text{m}^2\text{min})$. The furnace is lined with magnesite (MgO) bricks. For a batch run, the mass of pentoxide used is typically 1000 to 1200 kg Nb_2O_5 . Tapping of metal and slag is made into a cast-iron mold by tilting of the melting furnace. The melt is cooled in the mold for ~2.5 h, removed, and after an additional exposure for ~2 h, the metal and slag are delivered to a crusher.

The average consumption of the materials of 1 ton of Fe-50%Nb alloy is 758 kg of niobium pentoxide (base 100% Nb_2O_5), 385 kg of aluminum powder, 275 kg of iron ore (pellets), 86 kg of lime, and 31 kg of magnesite powder.

Respective composition of the slag is 70% to 75% Al_2O_3 , 9% to 12% CaO , 3% to 6% MgO , and 0.3% to 0.5% Nb_2O_5 , and during the solidification of the slag the mineral phases formed are, respectively, $\text{MgO}\cdot\text{Al}_2\text{O}_3$ (10% to 15%), $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ (75% to 85%), and $(\text{Ca},\text{K},\text{Na})\text{O}\cdot\text{Nb}_2\text{O}_5(\text{O},\text{F}) < 0.5\%$ to 3%. The properties of the slag after the grinding of the properties correspond to high-alumina refractory cements, and this slag is a valuable raw material for the production of high-alumina refractories.

The third method (melting in an arc furnace) is especially suitable for processing niobium-lean concentrates. It may have different versions, specifically the following:

1. Subsequent loading of the ore, aluminum, and flux mixture
2. Melting of the ore and flux of the mixture, followed by the addition of aluminum powder
3. Melting of the ore and flux mixture components with the subsequent addition of the remainder of the ore mixed with aluminum powder when the furnace power is off
4. Single-stage melting of a mixed charge together in an electric furnace to compensate for missing heat in the thermal balance.

The first method is characterized by low productivity of the furnace. Here, especially in the initial period, the interaction of the oxide with aluminum cannot be regulated. The degree of extraction of niobium does not exceed 70% to 80%, and the loss of aluminum as a result of oxidation reaches 30% to 40%.

The two-stage process is used for niobium ores containing high concentrations of tin (2% SnO_2) and phosphorus (0.15% P_2O_5). In the first melting stage, the slag is obtained with 47% ($\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$), 0.03% Sn, 0.04% P_2O_5 , and the metal containing 2.3% Sn, 0.06% P, and 3.3% ($\text{Nb} + \text{Ta} + \text{Zr} + \text{Ti}$). This option most completely utilizes the advantages of aluminothermic reduction by using electric power for the process and intensifying melting of the mixture with the required amount of flux (lime) to improve the extraction of niobium. In the second melting, a niobium-rich slag is mixed with lime and melted in an arc furnace, which also contains the molten iron scrap. Product FeNb alloy contains as average 66.2% Nb, 4.9% Ta, 0.02% Sn, 0.03% P, 0.2% Al, 1.0% Si, 2.3% Mn, and 0.004% S, and the final slag has 4.6% ($\text{Nb} + \text{Ta}$). The extraction of niobium in the alloy in the second stage is 95.2%, and the total extraction efficiency at these two stages is about 85%.

It is also possible to carry out one-step smelting of FeNb from pyrochlore concentrate, which is made in an electric arc furnace with a 3-ton capacity and lined with magnesite (MgO) bricks. After the furnace bath has been warmed, the mixture of 1000 kg of iron ore, 350 kg of recycled aluminum, and 200 kg of lime is arc-melted. The charge is composed of 100 kg of pyrochlore concentrate, 28 to 33 kg of recycled (secondary) aluminum powder, 3 to 10 kg of iron ore, and 5 to 12 kg of iron scrap. The first melting is carried out at 140 V. It takes 50 minutes to melt the 1200 kg concentrate charge; the second part with 1500

kg of concentrate takes 70 minutes, and the period with the subsequent charge of 1700 kg of concentrate takes 90 minutes. The cast-iron mold lined with MgO bricks for receiving the metal and slag is prepared during the previous smelting. The slag is partially tapped into the mold and cooled to form an autogenic lining layer, which is necessary to increase the durability of the mold and to obtain a clean surface of the ingot. After metal tapping, the mold is held for 2.5 h and after 2 more hours it is delivered for crushing and alloy extraction.

This method allows the production of FeSiNb with the composition of 56% to 62% (Nb + Ta), 10.7% to 12.5% Si, 2% to 6% Al, 3% to 8% Ti, 0.10% to 0.25% P, 0.05% to 0.15% C, and 0.004% to 0.5% S, and it can be applied in cases where high silicon content is not a limitation. However, as mentioned previously, excess silicon leads to the formation of high-temperature silicides (Nb_5Si_3), which delay dissolution of the alloy in the molten steel. To reduce the silicon percentage, FeSiNb can be purged with oxygen in the furnace, after tapping the process slag and setting new oxidation slag (niobium concentrate and lime), but this also reduces the extraction of niobium and part of it oxidizes and transfers back to slag.

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