Technology of Ferroalloys with Rare-Earth Metals

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18.1 PROPERTIES OF RARE-EARTH METALS AND THEIR COMPOUNDS

Traditional classifications of rare-earth metals (REM) include lanthanum ($z = 57$) and lanthanides (elements from cerium, $z = 58$, to lutetium, $z = 71$), with the addition of scandium ($z = 21$) and yttrium ($z = 39$) to this list (Table 18.1). Of these rare-earth elements, steelmaking technology mainly uses three of them, namely yttrium, lanthanum, and cerium, although in steels and ferrous alloys of this type all other REM might be present in various amounts. These three elements are considered in more detail in this section.

    The main function of REM in steels is to control the shape of nonmetallic inclusions (sulfides, silicates, oxides) remaining in killed and desulfurized steel (Trethewey and Jackman, 1981). REM have very high affinity for oxygen and sulfur, and thus may reduce other silicates and oxides (including Al_2O_3),

TABLE 18.1 Summary of the Properties of Rare-Earth Metals (Gasik et al., 2009)

Element	Atomic Mass	Valency (oxidation states)	Density, g/cm^3	Melting Temperature, K
Sc	44.96	3	3	1832
Y	88.9	3	4.47	1782
La	138.91	3	6.19	1193
Ce	140.12	3, 4	6.75	1077
Pr	140.91	3, 4	6.77	1208
Nd	144.24	3	7.01	1297
Pm	[147]	3	7.14	[1300]
Sm	150.35	2, 3	7.54	1325
Eu	151.96	3	5.24	1100
Gd	157.23	3, 5	7.87	1600
Tb	158.92	3	8.25	1700
Dy	162.3	3	8.56	1733
Ho	164.93	3	8.8	1773
Er	167.26	3	9.06	1800
Tm	168.93	3	9.32	1900
Yb	173.04	2, 3	9.96	1097
Lu	174.97	3	9.85	2000

forming rather hard globular inclusions (oxysulfides such as REM_2O_2S). The vapor pressure of REM at steelmaking temperatures is very small compared, for example, to calcium or magnesium, which have similar affinity for oxygen, and thus REM are much more efficient (yet more expensive) additions for steel deoxidation. Excess REM might also reduce refractory oxides from furnace and ladle lining, so their content must be controlled to achieve the desired effect. REM are generally very beneficial in hot-rolled steels as their presence decreases the anisotropy of properties due to the tendency to form globular inclusions. REM ferroalloys are also used in cast iron modification for the spheroidization of graphite (Cornell et al., 1981). Metallurgical applications account for about one third of the worldwide consumption of REM.

18.1.1 Yttrium

The element yttrium belongs to group III of the periodic table, as do all other REM. Natural yttrium is composed of one stable isotope. The configuration of the outer electron shell of yttrium is $4d^1 5s^2$, and its typical oxidation state is 3+. Yttrium has two allotropic forms: up to 1482°C the stable modification is α-Y (hexagonal lattice, a = 0.3647 nm) and it has a density of 4.45 g/cm^3. Above 1482°C, the stable modification is ß-Y (cubic lattice of α-Fe type, a = 0.408 nm). The melting point of yttrium is 1528°C, and the boiling point is ~3320°C. The vapor pressure at 1450°C is $6.5 \cdot 10^{-2}$ Pa.

Yttrium forms a very stable oxide Y_2O_3 (Fig. 18.1), which melts at 2430°C and boils at ~4300°C. It has a phase transformation at 2277°C, with lattice type change from cubic to hexagonal.
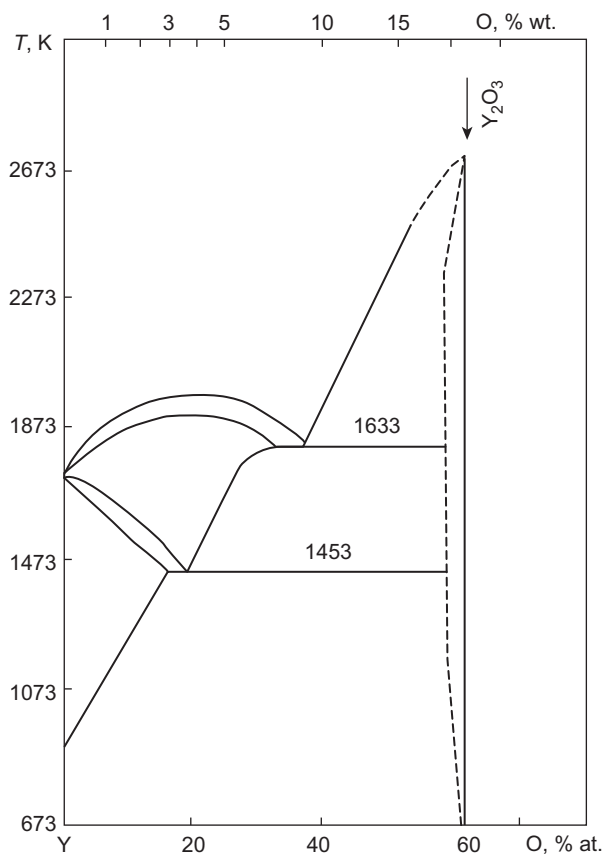

FIGURE 18.1   Diagram of the equilibrium state of the system Y-O.

With iron, yttrium forms several chemical compounds: YFe_9, also referred to as Y_2Fe_{17} (melting point ~1400°C); YFe_4, also referred to as Y_6Fe_{23} (melting point ~1300°C); and YFe_3 (melting point ~1400°C)—these all melt congruently. The YFe_2 compound melts incongruently at 1125°C. In yttrium-rich alloy eutectic is formed at 65.3% (at.) yttrium at 900°C. In the liquid state yttrium and iron form continuous solutions.

In the system Y-C, three carbides have been found (Fig. 18.2): YC, Y_2C_3, and YC_2. Y_2C_3 carbide is formed by the peritectoid reaction YC + $YC_2 \rightarrow Y_2C_3$ at ~1500°C. The eutectic contains ~15% (at.) C. Carbide YC (~40% at. C) has a small inhomogeneity range. Carbide YC_2 forms congruently at 2300°C.

The system Y-Si (Fig. 18.3) has four compounds (yttrium silicides): Y_5Si_3 (melting at 1850°C), Y_5Si_4 (melting at 1840°C), YS (melting at 1835°C), and Y_3Si_5 (incongruent melting temperature of 1635°C). The silicide YSi has an orthorhombic crystal lattice system with a density of 4.33 g/cm^3. In the system Y-Si eutectic, there are three eutectics: two with relatively low temperatures of 1260° and 1215°C, and one with a high temperature of 1710°C in the Y_5Si_3–Y_5Si_4 range. The solubility of yttrium in solid silicon is negligible.

18.1.2 Lanthanum

Lanthanum is a chemical element of group III, of the yttrium subgroup. Natural lanthanum is composed of two isotopes: stable La-139 (99.911%) and radio-active La-138 (0.089%) with a half-life period of $2 \cdot 10^{11}$ years. The electron
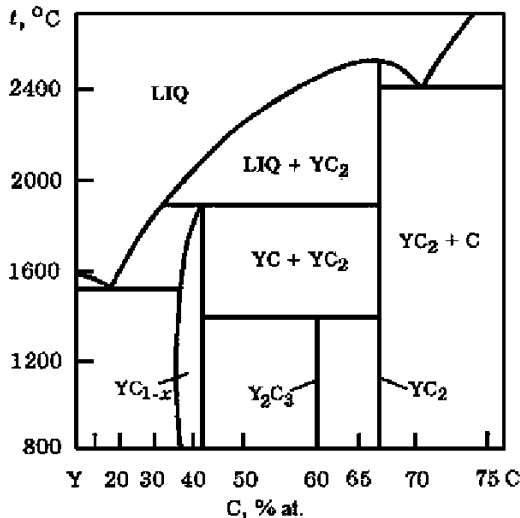

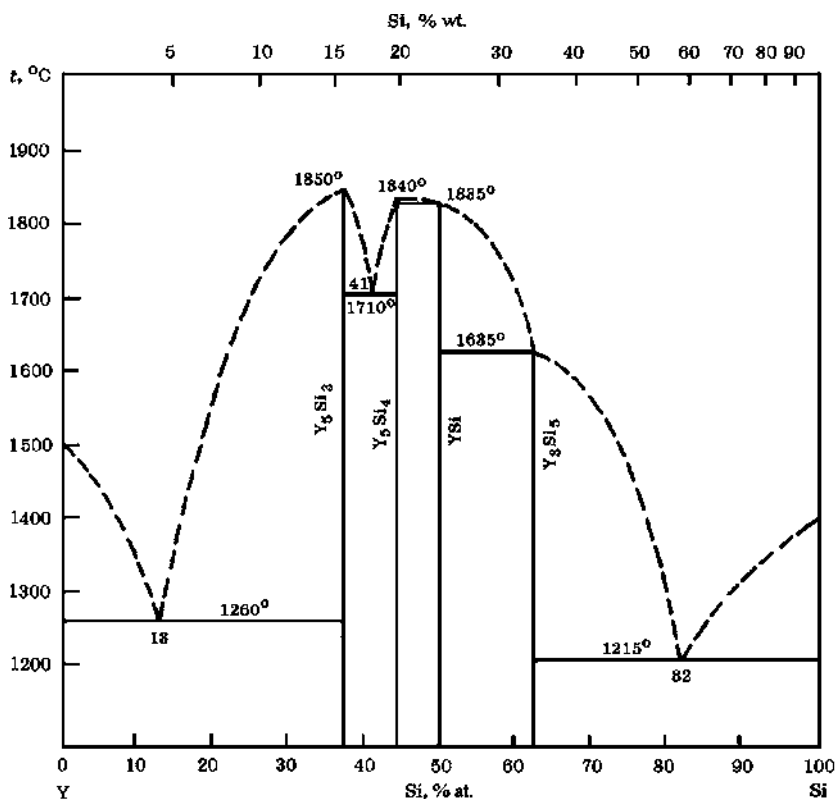**FIGURE 18.2**   Diagram of the equilibrium state of the system Y-C.

FIGURE 18.3   Diagram of the equilibrium state of the system Y-Si.

shell configuration of lanthanum is $5d^1 6s^2$, and its main oxidation state is 3+. At low temperatures ($<277°C$) the stable modification of lanthanum is α-La (hexagonal with a = 0.3772 nm, c = 1.2144 nm). In the range 277° to 861°C, ß-La with cubic lattice (a = 0.5296 nm) becomes more stable with a density of 6.19 g/cm^3. Within the 861° to 920°C range, the most stable modification is γ-La with an FCC lattice of α-Fe type (a = 0.426 nm) and a density of 5.97 g/cm^3. The melting point of lanthanum is 920°C, and the boiling point is 3454°C. With oxygen, lanthanum forms the stable oxide La_2O_3 with a melting point of ~2313°C.

Contrary to yttrium, lanthanum does not form compounds with iron and it has unlimited solubility in the liquid state. The solubility of lanthanum in the solid iron does not, however, exceed 0.1% (at.). The eutectic in this system forms at 785°C at 91.5% (at.) La.

With carbon, lanthanum forms carbides La_2C_3 and LaC_2 (Fig. 18.4), but not LaC (unlike in the Y-C system; see Fig. 18.2). LaC_2 carbide has a tetragonal crystal structure, a density of 5.35 g/cm^3, and a melting point of 2360°C.
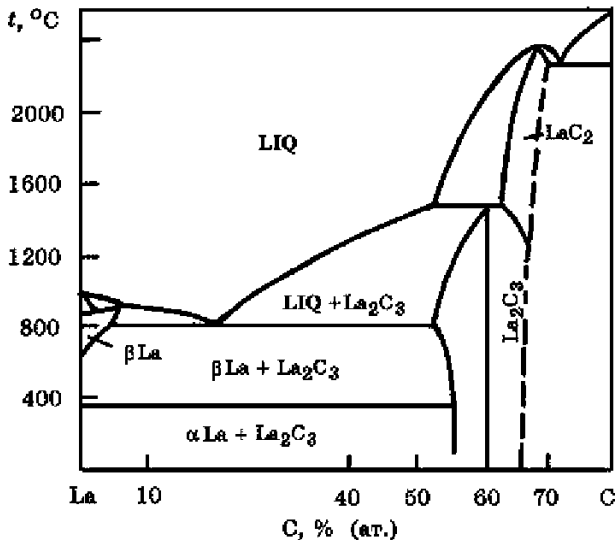
FIGURE 18.4   Diagram of the equilibrium state of the system La-C.

In the system La-Si, known compounds are LaSi, La_3Si_2, and $LaSi_2$. The melting point is assumed to be, for $LaSi_2$, 1520°C. This silicide crystallizes in the tetragonal crystal system and has a density of 5.05 g/cm^3.

18.1.3 Cerium

Cerium is also a chemical element in group III of the periodic table. Cerium starts the row of lanthanides (4f elements), as the configuration of the outer electron shells of the cerium atom is $4f^26s^2$. There are several known crystalline modifications of cerium. At room temperature α-Ce with a lattice of α-La type is stable. Between 61° and 727°C, ß-Ce is stable (FCC lattice of Cu type), and above this temperature γ-Ce (BCC lattice of W type) is stable.

Cerium forms two stable oxides, Ce_2O_3 and dioxide CeO_2 (Fig. 18.5). Oxide Ce_2O_3 is less stable (contrary to many other lanthanides and REM), and in the presence of O_2 is rapidly oxidized to CeO_2 with a large exothermic effect. Several intermediate phases with various oxygen contents have also been observed in this system, which makes cerium somewhat different from other lanthanides, with the exception of praseodymium.

The system Ce-Fe has two compounds, $CeFe_2$ and $CeFe_5$, which melt incongruently at 925° and 1060°C, respectively. There is also a eutectic with the coordinates of 14% (at.) cerium at 592°C. The formula of the $CeFe_5$ compound might be better described as Ce_2Fe_{17} (similar to Y_2Fe_{17}) with low- and high-temperature modifications.
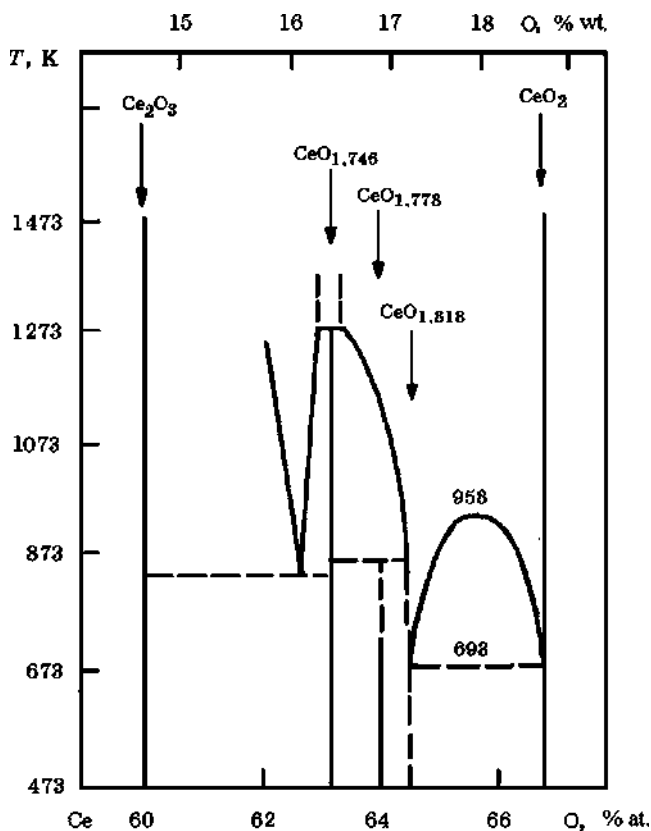
FIGURE 18.5   Diagram of the equilibrium state of the system Ce-O.

With carbon, cerium forms two stable carbides, similarly to lanthanum, namely CeC_2 and Ce_2C_3. The latter has a cubic lattice ($a = 0.844$ nm), and CeC_2 carbide has a tetragonal lattice and a density of 5.6 g/cm^3, melting at 2290°C. Ce_2C_3 carbide is formed by a peritectic reaction at temperatures above 1700°C.

With silicon, cerium forms several silicides, such as $CeSi$, Ce_5Si_3, and $CeSi_2$.

18.2 MINERALS, ORES, AND CONCENTRATES OF RARE-EARTH METALS

Contrary to their name, REM are relatively widespread in nature. For example, if the aluminum content in Earth's crust is taken as 100 units, the relative amount of REM would be 0.18, which is much greater than that for copper and cobalt (0.12), uranium (0.1), tungsten (0.060), or molybdenum (0.001). Rare-earth metals exist in the form of oxides, phosphates, carbonates,

fluorcarbonates, and other compounds. The main minerals containing rare-earth metals are bastnaesite (Ce, La)[FCO_3], with a density of 4.2 to 5.2 g/cm^3, and monazite (Ce, La, Nd, Th)[PO_4], which also contains impurities such as ThO_2 (10%), UO_2 (6,6%), and ZrO_2.

Monazite is most common in pegmatite rocks and it is used as a raw material for cerium and thorium extraction. Loparite is a mineral of the fluorcarbonate group with the formula $Ca(Ce,La)_2[CO_3]F_2$ and it contains 30.5% Ce_2O_3, 10.44% CaO, and 24.58% CO_2. Minerals of pyrochlore groups have the general formula $(Ca, Na, U, Ce, Y)_{2-m} \cdot (Nb, Ta, Ti)_2O_6(OF)_{1-m} \cdot H_2O$ and usually are associated with other similar minerals, rich in REM, tantalum, uranium, titanium, and other elements (Gasik et al., 2009).

The main industrial sources of rare-earth metals are bastnaesite, monazite, and xenotime. The first of these forms its own deposits; the other two usually present as minor components with ilmenite, rutile, zircon, and other minerals. Additionally, some REM might be extracted from specific sources (e.g., about 16% of yttrium comes from uranium ore waste). The leading REM producers are China, the United States, Brazil, and India.

Ores with minerals containing rare-earth metals are usually subjected first to a gravity separation step to isolate heavy minerals—monazite, xenotime, and so on. Monazite is further extracted from a mixture with a combination of gravitational, electromagnetic, and electrostatic methods. Chemical methods of processing concentrates include leaching and separation of radioactive impurities and the REM themselves, ensuring at the end the attainment of pure RE metals. Bastnezite concentrate is leached with hydrochloric acid, which allows the isolation of cerium concentrate from the nondissolved precipitate. Loparite concentrates are processed via chlorination. Recent monazite and bastnezite concentrates contain, respectively, about 60% and 70% wt. of rare-earth oxides. The mass fraction of each element of the rare earth in those concentrates is typically as shown in Table 18.2.

18.3 TECHNOLOGY FOR PRODUCING FERROALLOYS WITH REM

Some REM are produced in their pure form, usually by a reduction of extracted and purified fluoride salt by aluminum, but sometimes by calcium, magnesium,

TABLE 18.2 Typical Breakdown of REM in Different Mineral Concentrates, % wt.

REM Type	La	Ce	Pr	Nd	Sm	Eu
Monazite concentrate	22	45	5.6	17.8	3.2	0.1
Bastnaezite concentrate	34	50	4	11	0.5	0.1

or sodium. The obtained ingot is refined by vacuum remelting, but such production is not on a large scale.

The mixed alloy ("mischmetal," >98% wt. REM) and in some cases fer-rocerium (>85% REM; mainly of the Ce group) are commonly produced by electrolysis of molten REM chloride and fluoride salts. Alkali chlorides are added to the melt and the composition of reduced metal at the cathode is roughly proportional to the composition of the chloride melt. The electrolysis is carried out in steel reactors (walls serve as the cathode) with graphite rods (the anode) at 800° to 900°C. The resulting mischmetal alloy contains usually (wt. %): >45 Ce, 23–26 La, <20 Nd, and <10 other REM and impurities such as iron and aluminum. The electrolysis process has, however, a high energy consumption and limited applicability.

For steelmaking applications, ferroalloys with REM are the most common product (Oprea et al., 1989). As mentioned previously, these ferroalloys are mostly used to modify the structure of nonmetallic inclusions. The nominal grades of Fe-REM alloys commonly produced are shown in Table 18.3 (all of these alloys have 30% to 50% wt. Si and a balance made up of Fe). These alloys have been recommended to be used in the lump form with size below 20 to 30 mm to ensure their better utilization in steelmaking (Vichlevscuk et al., 1990).
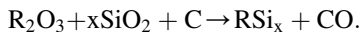
18.3.1 Reduction by Carbon

Lean REM ferroalloys (<15% REM) can be produced by carbon reduction. These REM ferroalloys with a high percentage of silicon are normally produced in ore-reduction ovens using a continuous smelting method. The charge contains a concentrate with REM, quartzite, carbon reductant, and steel chips. The exact dosing of carbon is of particular importance for the reduction of silicon and rare earths (R), as deviations of the carbon amount in the charge

TABLE 18.3 Approximate Composition of Fe-Si-REM Alloys

Fe-REM	% wt. REM	% Al	
		For Reduction by C	For Reduction by Al
FeSi-30REM	30-40	2-4	4-8
FeSi-20REM	20-30	2-3	3-6
FeSi-15REM	15-20	2-6	6-10
FeSi-10REM	10-15	2-3	3-6
FeSi-5REM	5-10	2-8	6-15

would cause an undesirable formation of accretions at the bottom of the furnace (SiC, RC, RC_2, unreduced R_2O_3, and SiO_2) and a decrease of REM recovery.

The general reaction of REM reduction by carbon might be presented as follows:

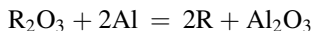$$R_2O_3 + xSiO_2 + C \rightarrow RSi_x + CO.$$

This reaction usually develops over 2000 K. REM recovery is facilitated by reducing their thermodynamic activity due to the formation of their solution with silicon and iron. In the ferroalloy with 30% to 40% REM, the rare-earth metals are in the silicide form. Reduction processes are accompanied by the formation of oxycarbides and carbides.

The increase of REM content in the ferroalloy leads to a drop of the extraction degree of these metals due to the formation of gaseous oxides (RO) and to an increase in the amount of slag. The density of the slag with increasing silicon content in the alloy is close to the density of the metal melt, and this may lead to difficulties in slag/metal separation. It is advisable to keep REM content in the molten alloys at 35% to 45% wt. REM, as in this case an REM utilization of 75% to 85% could theoretically be reached. It also leads to better utilization of REM in steelmaking and processing of modified cast iron.

18.3.2 Reduction by Aluminum

To obtain a significant number of REM-containing ferroalloys with low carbon content and without the risk of accumulating carbide accretions, the reduction of REM oxides by aluminum has been developed. In this case, the general reaction might be written as

$$R_2O_3 + 2Al = 2R + Al_2O_3$$

and the Gibbs energy change (ΔG) for this process is usually positive in the standard state for practically achievable process temperatures (only cerium might be theoretically reduced to a pure metallic state by aluminum). Therefore, to achieve a sufficient degree of REM reduction, an excess amount of aluminum in the charge is required. Commonly $>100\%$ of the theoretically necessary aluminum is added to the charge, and this will lead to formation of master alloys with 3% to 7% Al and a significant amount of silicon. Altogether this creates favorable conditions for the reduction of REM activity during their dissolution in the melt.

The process is carried out in an electric arc furnace (power rating 1.8 MVA) with a hearth and walls lining made of carbon. The charge includes a concentrate of REM (yttrium or cerium subgroup) and a lanthanum oxide concentrate containing 40% to 47% CeO_2 and 41% to 48% ($La_2O_3 + Nd_2O_3 + Pr_2O_3$). Reductant is a primary or secondary aluminum powder (depending on the required chemical composition of the alloy). Additionally the charge contains ferrosilicon FeSi75, low-phosphorus iron ore concentrate ($>63\%$ Fe), and

fluxes (fresh lime and fluorspar). Per 100 kg of REM concentrate, 32 to 41 kg of aluminum powder are consumed, plus 110 to 125 kg of ferrosilicon, 30 to37 kg of lime, and 0 to 5 kg of iron concentrate and fluorspar.

The charge is loaded after setting up the electric load. The charge is divided into two parts; the first has 55% to 75% concentrate, 60% to 65% lime, 60% ferrosilicon, and 42% aluminum powder (of their total amounts per batch). After this first part is melted and soaked for 5 to 7 min under constant current, the second part of the charge is loaded. Upon the completion of the melting process, slag is tapped into a lined ladle and the metal into a cast iron mold.

The metal (see Table 18.3) contains 11% to 40% rare-earth metals, 33% to 52% Si, 7% to 9% Al, 5% to 6.3% Ca, 0.01% to 0.03% C, and 12% to 20% Fe, and it has a density in the range 3.3 to 3.9 g/cm^3. Because the slag density is 3 to 3.6 g/cm^3, such small differences can cause extra losses of REM with the slag. An injection of fluorspar and sodium chloride is used to improve the separation of metal and slag—this decreases the density of the slag.

To produce 1 ton of the Fe-Si-REM ferroalloy, the following consumption of raw materials is observed: 520 to 565 kg of REM oxides concentrate, 203 to 210 kg of aluminum powder, 225 kg of lime, 630 to 695 kg of Fe-Si75, and 30 to 35 kg of iron ore. The energy consumption is 2100 to 2200 kWh/t of the alloy.

It is also possible to produce REM alloys in two stages, where the first reduction is carried out by silicon and the second is carried out by aluminum. The studies have shown a high degree of extraction of rare-earth elements in the metal (92% to 97%) and the possibility of obtaining lime–alumina slag with a low content of oxides of REM (1.6% to 4.8%). The development of the technology of melting alloys with rare earths offers the possibility of reducing the cost of 1 ton of alloy (30% REM). The lime–alumina slag (50% to 60% Al_2O_3, 35% to 40% CaO, and up to 5% rare-earth oxides) can be effectively used for secondary treatments.

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