

Technology of Chromium and Its Ferroalloys

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8.1 PROPERTIES OF CHROMIUM

Chromium is element no. 24 of the IVb subgroup of the periodic table, along with its analogs molybdenum and tungsten. It has atomic mass 51.996 and an external electron configuration of $3d^54s^1$, leading to stable valences of +2, +3, and +6. Chromium's density is 7.19 g/cm³, its melting temperature is 1870°C, and its boiling point is about 2469°C. Chromium has BCC lattice, which is stable throughout the range of solid chromium stability (i.e., it does not have stable phase transformations in the solid state).

Chromium is one of the most versatile and widely used alloying elements in many steels and alloys. It imparts corrosion and oxidation resistance, is a mild hardenability agent, improves wear resistance, and promotes the retention of useful strength levels at elevated temperatures. Chromium is the basis of all stainless steels (about 70% of all chromium used in steelmaking belongs to stainless steels). It is also an important part of low-alloyed constructional alloy steels (1% to 3% Cr) and ball-bearing steels. Chromium is also used in various tool steels, superalloys, and other specialty metals. Besides chromium's ability to form protective oxide (Cr_2O_3), which is the main reason for its use in stainless steels, it forms hard carbides, which are employed in wear-resistance applications.

8.1.1 Phase Equilibria with Major Chromium-Containing Systems

Carbon and chromium form several carbides, which have been a subject of many investigations. The commonly observed carbides in the Cr-C system are $Cr_{23}C_6$ (5.68 wt. % C; sometimes also referred as Cr_4C), Cr_7C_3 (9% C), and Cr_3C_2 (13.3% C). The types of crystalline lattices and their parameters for chromium carbides have been determined as complex BCC for $Cr_{23}C_6$ ($a = 1.066$ nm), hexagonal for Cr_7C_3 ($a = 1.401$, $c = 0.425$ nm), and orthorhombic for Cr_3C_2 ($a = 1.147$, $b = 0.5545$, $c = 0.283$ nm) (Bolgar et al., 1973). Chromium carbides have more complex crystalline structures than the carbides of Ti, Zr, V, or Nb. Additionally, metastable chromium carbide has been identified to form in binary Cr-C alloys at rapid solidification or quenching (Inoue and Matsumoto, 1979). This Cr_3C carbide has a structure similar to that for metastable iron carbide (cementite Fe_3C) with lattice parameters $a = 0.458$ nm, $b = 0.512$ nm, and $c = 0.680$ nm. The Cr-C phase equilibria diagram is shown in Figure 8.1. The solubility of carbon in solid chromium is low (Lyakishev and Gasik, 1998; Zemskij and Fokin, 1967).

With oxygen, chromium forms a wide range of oxide phases with different molar ratios Me:O from 3:1 to 1:3, which is typical for its analogs (Mo and W). These oxides have different thermal stability. High-oxygen compounds (Me:O < 2:3, such as CrO_3 , Cr_8O_{21} , Cr_5O_{12} , and CrO_2) dissociate almost completely already at relatively low temperatures and thus are not relevant to

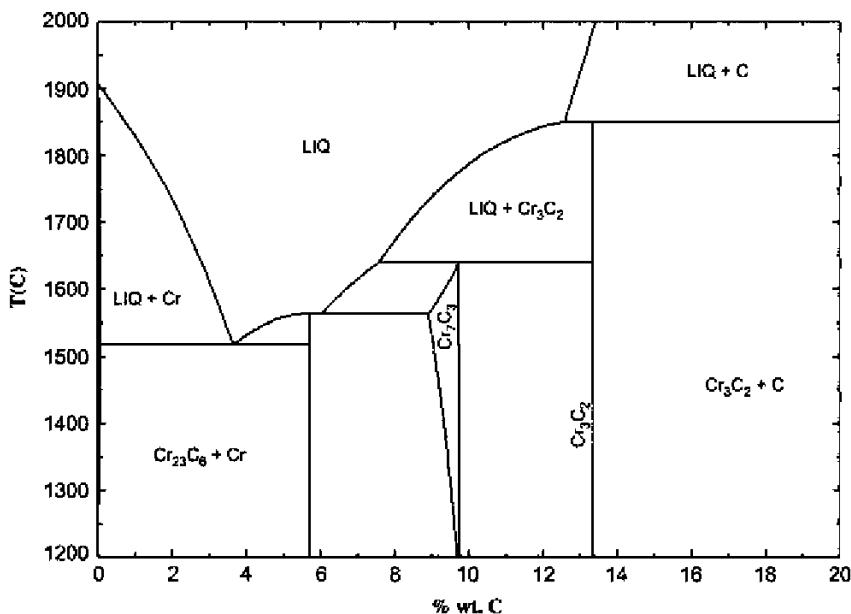


FIGURE 8.1 The carbon–chromium phase equilibria diagram.

ferrochromium processing, although they may form during cooling of Cr-containing gases and fumes or the oxidation of chromium-rich alloys. These intermediate oxides are sometimes considered to be chemical compounds of chromium chromate and polychromates. For example, Cr_5O_{12} might be presented as $\text{Cr}_2(\text{CrO}_4)_3$, $\text{Cr}_6(\text{Cr}_{10}\text{O}_{30})$, and $\text{Cr}_4(\text{Cr}_7\text{O}_{27})$ (Lyakishev and Gasik, 1998; Rode, 1962).

The stability of oxides increases with an increasing Me:O ratio with trivalent chromium oxide Cr_2O_3 being the most stable. Oxides Cr_3O_4 (tetragonal lattice of rutile-type with $a = 0.4421$ and $c = 0.2916$ nm) and CrO (cubic lattice with $a = 0.412$ nm) are stable at high temperatures only. Upon cooling they usually decompose to Cr and Cr_2O_3 . Oxide Cr_3O_4 might be also considered as a chromium chromite, CrCr_2O_4 or $\text{CrO} \cdot \text{Cr}_2\text{O}_3$. The practically relevant oxide Cr_2O_3 has the structure of corundum $\alpha\text{-Al}_2\text{O}_3$ type, but was also found to have a tetragonal lattice when it exists in the form of mineral eskolaite (Lyakishev and Gasik, 1998).

Oxygen solubility in solid chromium is low (~0.013 wt. % O at 1500°C), and oxygen lowers chromium's melting point. A version of the phase diagram of the Cr-O system is shown in Figure 8.2.

The oxide liquid phase may form over 1663°C in equilibrium with either chromium or chromium oxides. Over 1875°C two liquids (metal-rich and oxide-rich “ CrO ”) might co-exist in a wide range of oxygen compositions. Note that the explicit appearance of “ CrO ” at the phase diagram depends on

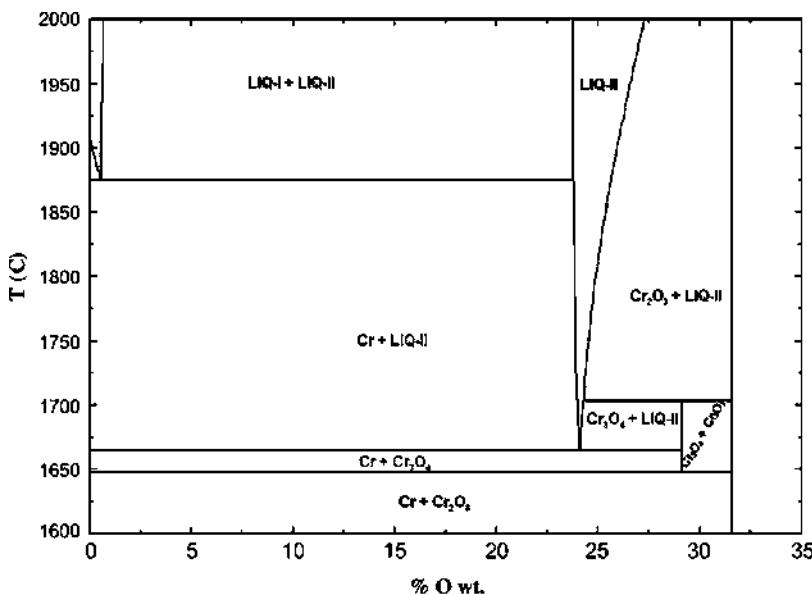


FIGURE 8.2 The phase diagram of the Cr-O system.

the selection of the gas phase, especially oxygen potential (Fig. 8.3). For theory as well as the practice of producing alloys of the Cr-Fe system (FeCr and chromium-rich steels), the thermodynamic properties of chromium monoxide (CrO) are also of interest. This oxide is usually stabilized in the presence of silica (acidic slags), where the ratio $\text{Cr}^{3+}/\text{Cr}^{2+}$ is decreasing (Gasik et al., 1970; Lyakishev and Gasik, 1998). This might be shown in the Cr-O phase dominance diagram as function of temperature for the Cr-O system (see Fig. 8.3). Here chromium oxides are supposed to be pure phases and the theoretical stability area of the CrO in this binary system appears to be in this case over 1710°C and in the limited range of equilibrium oxygen potentials.

For chromium reduction from oxides, thermodynamics of the Cr-O-C equilibria is of high importance. Let's consider the isothermal sections of this phase dominance diagram for different temperatures (Fig. 8.4). Here cross marks (+) indicate the isobar line—the total pressure in the system, which was fixed to be 1 atm. If these cross marks exist anywhere in the phase stability field, this means there is a thermodynamic possibility of obtaining this phase in the system.

Table 8.1 shows numerical data of these equilibria. Here the equilibrium type means only these phase areas, which are being crossed by the isobar line (Fig. 8.4 shows the coordinates of the crossing points as logarithms of partial pressures of CO and CO_2). The respective triple points (if they exist) are

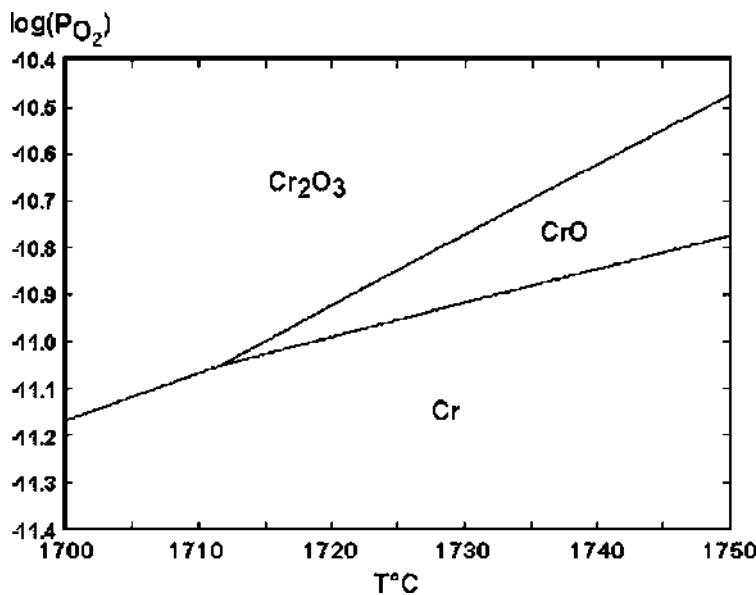


FIGURE 8.3 Triple point in the Cr-O system at high temperatures (calculated with HSC Chemistry ver. 7.1).

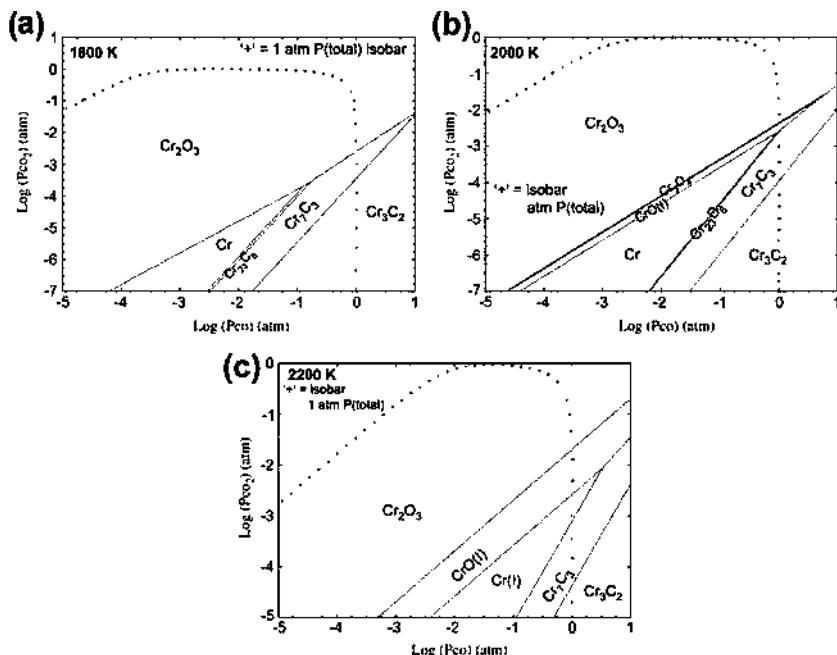


FIGURE 8.4 Phase stability diagram for the Cr-C-O system at 1800 (a), 2000 (b), and 2200 K (c).

TABLE 8.1 Types of Equilibria in the Cr-O-C Systems at Different Temperatures

T, K	Equilibrium Type	$\log P_{CO}$	$\log P_{CO_2}$	Invariant point	$\log P^*_{CO}$	$\log P^*_{CO_2}$
1800	$Cr_3C_2-Cr_7C_3$	-0.000926	-3.44615	$Cr-Cr_7C_3-Cr_2O_3$	-1.18413	-4.04745
	$Cr_7C_3-Cr_2O_3$	-0.000926	-2.59538			
2000	$Cr_3C_2-Cr_7C_3$	-0.000694	-3.95231	$Cr-Cr_7C_3-Cr_3O_4$	-0.11428	-2.68805
	$Cr_7C_3-Cr_3O_4$	-0.000694	-2.54154	$Cr_2O_3-Cr_7C_3-Cr_3O_4$	0.80694	-1.53731
	$Cr_3O_4-Cr_2O_3$	-0.000694	-2.34410			
2200	$Cr_3C_2-Cr_7C_3$	-0.031746	-4.37345	$Cr-Cr_7C_3-Cr_3O_4$	0.74921	-1.5993
	Cr_7C_3-Cr	-0.031746	-3.11248			
	Cr_3O_4-Cr	-0.031746	-2.35589			
	$Cr_3O_4-Cr_2O_3$	-0.031746	-1.75923			

summarized with their coordinates. Note that triple points might not be located at the isobar line, and this means they will not be accessible at these temperatures at ambient total pressure.

The conclusions one could make on the basis of these diagrams are as follows. First, at 1800 K it is not possible to get metallic chromium in the Cr-C-O system but only oxide Cr_2O_3 (at high CO_2 fractions) or carbides Cr_23C_6 and Cr_3C_2 (at high CO fractions) if the total system pressure of 1 bar (atm) is maintained. According to the data in Figure 8.3, an increase of temperature to 2000 K leads to the appearance and extension of the Cr_3O_4 and CrO areas. At the even high temperature of 2200 K, CrO seems to not be stable anymore, as metallic chromium is now possible (yet within a very limited range of pressure of CO_2). Therefore, even though chromium might be reduced by carbon at high temperatures and normal pressure, it is unlikely to be practically feasible for pure metal production due to difficulties in local control of the gas atmosphere. Furthermore, these diagrams do not explicitly show that in these conditions a significant part of the chromium compound is present in the gas phase. Thermodynamics of the Cr-C-O equilibria justifies that the most practical method of chromium reduction by carbon might be realized by decreasing chromium activity in the melt with the addition of iron or silicon.

The system Cr-Si has been studied for many years and several compounds have been reported: Cr_2Si , Cr_3Si_2 , $CrSi$, Cr_2Si_3 , $CrSi_2$, and Cr_2Si_7 . Later, not all of them were confirmed and reliable data exist for Cr_3Si , Cr_5Si_3 , $CrSi_2$, and to some extent $CrSi$. Depending on the thermodynamic data used, different versions of the Cr-Si phase diagram have been published. One of the versions as calculated by the authors is shown in Figure 8.5. The solubility of chromium in solid silicon is very low (possibly <0.06 ppm below 1300°C),

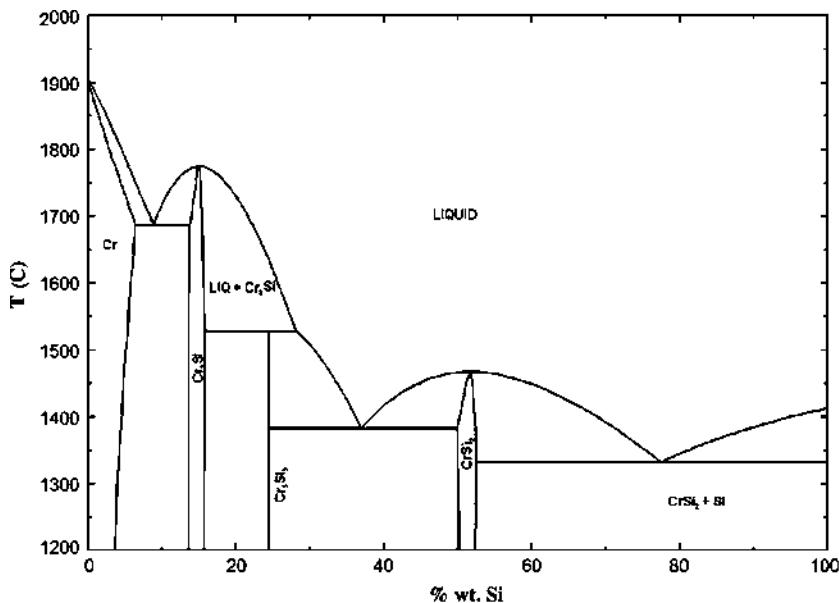


FIGURE 8.5 Phase diagram of the Cr-Si system.

but solubility of silicon in solid chromium is of an order of 1.36% wt. at 1650°C.

In the ternary system, Cr-Si-C besides carbides and silicides (including SiC), a ternary nonstoichiometric compound (known as the Nowotny phase), Cr₅Si₃C_x, is also formed. The crystalline lattice of the Cr₅Si₃C_x is more defective and includes fairly large voids. Saturation of Cr₅Si₃ with carbon results in the formation and stabilization of the hexagonal Cr_{5-x}Si_{3-y}C_{x+y}. Saturation of binary Cr-Si alloys with carbon gives not only Cr₅Si₃C_x but also carbides Cr₇C₃ and Cr₃C₂. Only the silicides CrSi and CrSi₂ do not change their structure after carburization. In carbon-saturated alloys at a constant temperature, the carbon solubility is a linear function of silicon content. The formation of SiC occurs when a melt is oversaturated with carbon on the liquidus surface. Having lower density, SiC is precipitated at cooling and segregates up to the surface of the melt.

In the presence of iron, these phases have been reported as (Cr, Fe)₁₄Si₄C₃ (15% to 18% wt. Fe) and (Cr, Fe)₅Si₃C₆ (23% to 30% wt. Fe) (Kosyrev and Olsen, 1995). These phases appear in equilibria in the carbon-saturated Cr-Fe-Si melts (Fig. 8.6) and play an important role in all chromium ferroalloys processing where reduction by carbon and silicon is involved.

In the chromium-nitrogen system, two stable nitrides are known: Cr₂N (β -phase, HCP lattice type with $a = 0.4582(\pm 3)$, $c = 0.4460(\pm 20)$ nm) and CrN (γ -phase, cubic structure with $a = 0.415$ nm) (Fig. 8.7). The nitride Cr₂N has

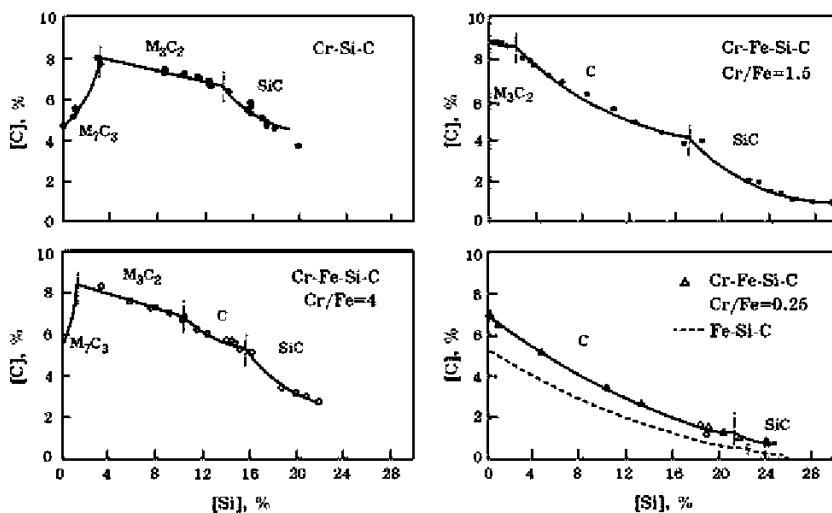


FIGURE 8.6 Phase equilibria and solubility of carbon and silicon at 1600°C in the Cr-Fe-Si-C system (Gasik et al., 2009).

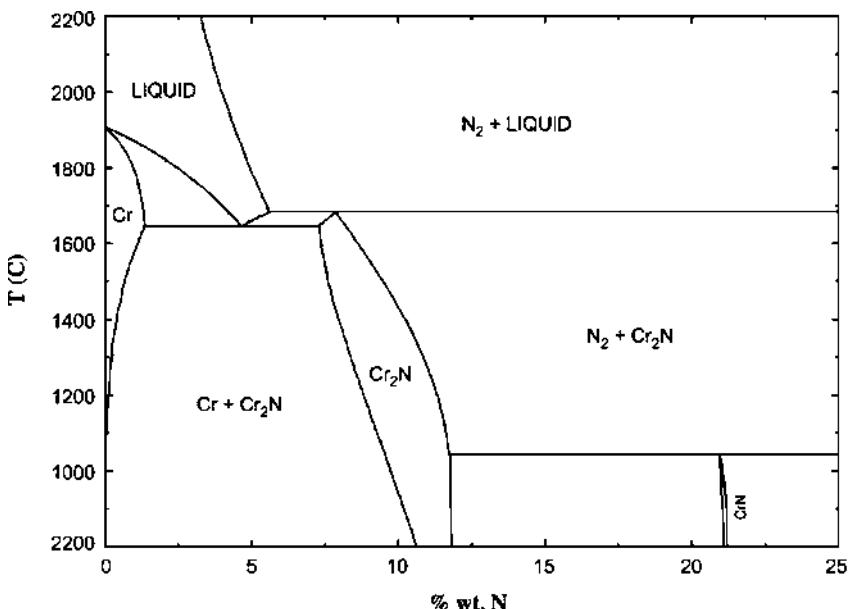


FIGURE 8.7 Phase diagram of the Cr-N system at 1 atm pressure of nitrogen.

a homogeneity region in the range 11.3 to 11.9 wt. % N. Nitride CrN is nearly stoichiometric with a high enthalpy of formation, which makes its thermal stability compatible with nitrides like TaN. Nitrogen dissolves in solid chromium in small amounts. The equilibrium nitrogen content in liquid chromium is higher than in solid chromium, but it decreases with temperature due to the exothermal nature of the reaction of interaction of molecular nitrogen with chromium melt. The dissolution of nitrogen in chromium significantly lowers its melting point (eutectics ~1650°C; see Fig. 8.7).

During the reaction of nitrogen with metallic chromium at 960° to 1200°C and $P_{N_2} = 1$ to 2 MPa, it is also possible to form a nonstoichiometric nitride Cr_2N_x ($x < 1$) (Lyakishev and Gasik, 1998). Such specimens with 8 to 11 wt. % N usually have a multiphase structure with a solid solution of nitrogen in Cr, Cr_2N , CrN, and Cr_2N_x . The latter phase does not form at nitrogen concentrations >11% wt. The Cr_2N_x phase is assumed to be the product of the disproportion of Cr_2N with the formation of a nitrogen-lean solid solution based on the Cr_2N lattice.

With phosphorus chromium forms several phosphides (Cr_3P , Cr_2P , CrP , CrP_2), which are stronger than similar phosphides of iron. The solubility of phosphorus in solid chromium is low, and phosphorus removal from the chromium-rich melts by oxidation is not efficient.

Sulfur forms stable chromium sulfides CrS , Cr_3S_4 , and Cr_2S_3 , as well as two metastable sulfides, Cr_7S_8 and Cr_3S_6 .

For the equilibrium of chromium with other metals, iron and aluminum are the most important cases. The Fe-Cr system is one of the basics for ferrochromium and chromium steel production, and it forms a basis for the whole study of chromium metallurgy (Lyakishev and Gasik, 1998; Mills and Grieveson, 1976; Witusevich et al., 1987). The Fe-Cr phase equilibrium diagram is shown in Figure 8.8.

The maximum solubility of chromium in the iron-rich γ -FCC phase is observed at ~980°C at 11.4 wt % Cr. When chromium exceeds ~13.5 wt. % Cr, only the α -BCC phase is stable (see Fig. 8.8). The positions of the phase boundaries are affected considerably by the impurities present, such as nitrogen and carbon.

The BCC solid solutions of the Fe-Cr system near equimolar composition tend to form the σ -phase. It exhibits a tetragonal crystalline lattice ($a = 0.8800$, $c = 0.4544$ nm) at a nominal content of 46.5 at. % Cr. This phase is usually considered to be undesirable in the Cr-rich steels and alloys as it causes excessive brittleness. The σ -phase exists in equilibrium with three types of BCC solutions: α -phase (ferrite) at apex, α' (iron-based ferrite), and α'' (chromium-based ferrite). They all have the same BCC structure but different composition and lattice parameters. The experimental validation of such transformations is always challenging, as it requires a long equilibration time—for example, equilibration times of even 11 years at 500°C have been reported (Zubkov et al., 1990).

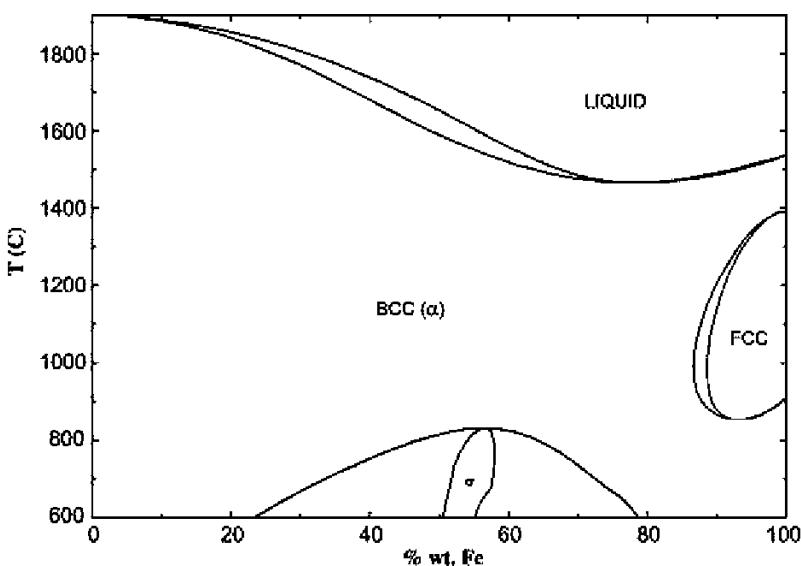


FIGURE 8.8 Phase diagram of the Cr-Fe system.

The chromium-aluminum equilibrium is important for processing metallic chromium by reduction of the oxide with aluminum. This system has several intermetallic compounds (Fig 8.9). Some of these phases described by exact stoichiometric ratios could be represented by other ratios of chromium and aluminum atoms. The solubility of Al in BCC chromium is rather broad, but solubility of chromium in FCC aluminum is limited to ~0.5 wt.% Cr at a peritectic equilibrium of 651°C.

8.1.2 Phase Equilibria with Chromium Oxide

In the $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ system, chromium oxide does not form intermediate phases with alumina, given that a region of continuous solid solutions exists below the solidus line, at least above 1500 K. At lower temperatures, the solid solution tends to decompose into two isomorphic chromia-rich and alumina-rich solutions. The region of coexistence of these two solutions is about from 15% to 25% to 50 to 70 mol. % Cr_2O_3 , but the exact phase boundary positions remain the subject of discussion.

Reliable data on the phase equilibria in the chromia-silica system and the presence of metallic chromium in contact with the silicate melts are important for optimizing the slag modes of reducing processes in the production of chromium ferroalloys. These data are of a great theoretical and practical interest for the production of chromium-containing steels and oxidative decarburization of high-carbon ferrochromium in converters. Under the

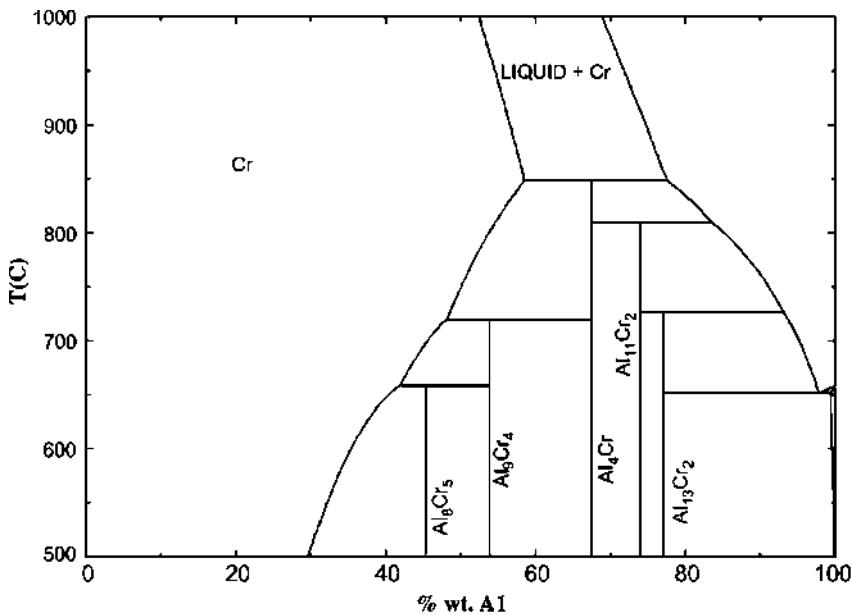


FIGURE 8.9 Phase diagram of the Cr-Al system.

conditions of a high oxidative potential of the gaseous phase and the absence of a metallic chromium-containing melt, silica does not react with Cr_2O_3 .

In reducing conditions (a low oxidative potential of the gaseous phase and the presence of metallic chromium), the interaction of silica with chromium oxide (Cr_2O_3) is accompanied by the reduction $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$, followed by the formation of, a silicate melt “ CrO ”- SiO_2 . Here a hypothetical phase diagram (Fig. 8.10) shows where “ CrO ” oxide is used instead of Cr_2O_3 . As shown for the Cr-O system, in purely acidic (silica-rich) environments, the ratio $\text{Cr}^{3+}/\text{Cr}^{2+}$ is substantially decreased, leading the Cr^{2+} form to be in equilibrium with silica-rich melts. As CrO is not an independent stable phase at normal conditions, it is described by the $\text{Cr}_2\text{O}_3 + \text{Cr}$ composition in silica-lean areas. Figure 8.10 also shows the region of existence of chromium silicate Cr_2SiO_4 . Although approximate, it explains some of the technological methods employed in the production of chromium ferroalloys and steels.

The opposite of silica, calcia as a basic oxide shifts equilibria toward higher chromium valences in the presence of oxygen. CaO forms calcium chromite (CaCr_2O_4) with Cr_2O_3 at high temperatures in the chromium-rich area (Fig. 8.11). This chromite is not stable at lower temperatures and its composition also has been reported as $(\text{Ca}_2\text{Cr}_3)\text{Cr}_{10}\text{O}_{20}$ —that is, as mixed calcium-chromium chromite (Dechterov and Pelton, 1997). Upon the increase of CaO content, the ratio $\text{Cr}^{6+}/\text{Cr}^{3+}$ gets higher and calcium chromate CaCrO_4 is formed. Further, two more complex compounds (calcium chromite-chromates)

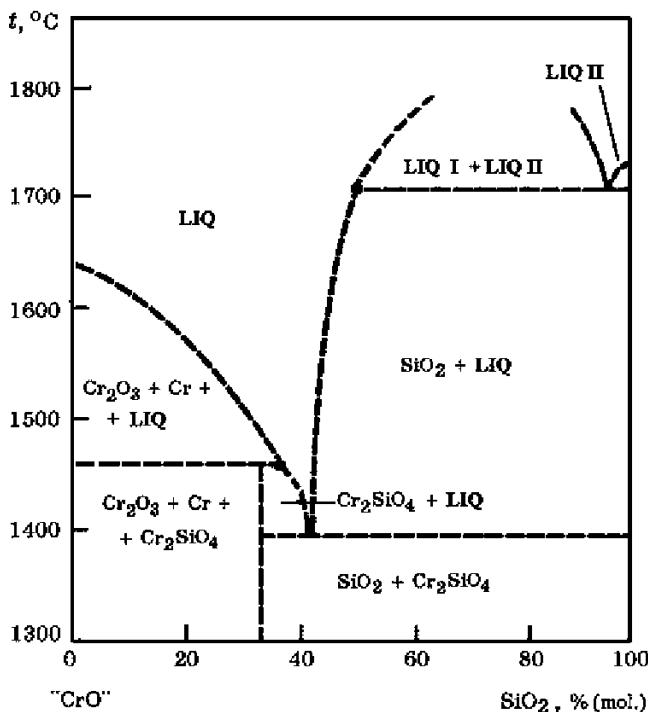


FIGURE 8.10 The “CrO”- SiO_2 phase diagram.

of composition $9\text{CaO} \cdot 4\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ and $3\text{CaO} \cdot 2\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3$ have been identified. It was also suggested that this diagram should be treated as a part of the ternary equilibrium $\text{CaO-Cr}_2\text{O}_3-\text{CrO}_3$ (Kaiser et al., 1992; Lyakishev and Gasik, 1998). For example, Kaiser et al., (1992) identified compositions $\text{Ca}_5(\text{CrO}_4)_3\text{O}$ to be stable in air between 776° and 959°C , $\text{Ca}_3(\text{CrO}_4)_2$ between 882° and 1253°C , and $\text{Ca}_5(\text{CrO}_4)_3$ between 1140°C and 1297°C , but unstable in reducing conditions.

The substantial decrease of the liquidus temperature ($<1775^\circ\text{C}$) in a range of compositions (30% to 60% Cr_2O_3) is utilized for calcia-chromia melts processing during low-carbon FeCr production by mixing FeSiCr and $\text{CaO-Cr}_2\text{O}_3$ melts.

Besides equilibria of chromia with CaO and SiO_2 , the system $\text{Cr}_2\text{O}_3-\text{MgO}$ is one of the most important systems in the production of ferroalloys and steels. In this system only one compound (magnesium spinel MgCr_2O_4) is formed, but MgO has a wide solubility range, decreasing with lower temperatures (Fig. 8.12). Magnesium chromite was also reported to have some homogeneity range.

The binary systems with Cr_2O_3 discussed previously do not explicitly appear as such in ferroalloys processes but they form a basis for ternary and

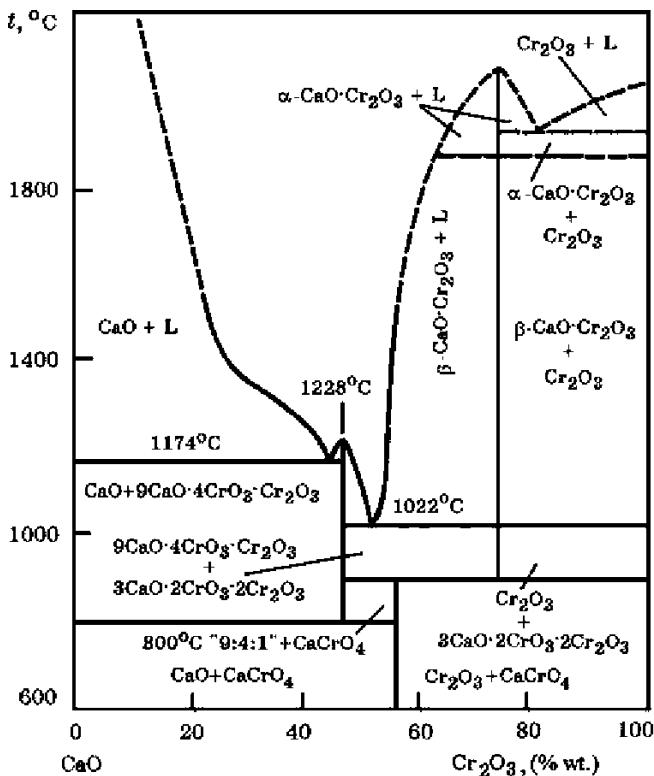


FIGURE 8.11 The CaO-Cr₂O₃ phase diagram.

more complex combinations. The most important ones are briefly presented in this chapter.

In the ternary system Cr₂O₃-Al₂O₃-SiO₂, a large region of corundum solid solutions and also a narrow long field of mullite (3Al₂O₃·2SiO₂) have been reported (Lyakishev and Gasik, 1998). The triple eutectic liquid composition has 6% wt. Al₂O₃ and 1% wt. Cr₂O₃. Eventually no ternary compounds appear in equilibrium here. Due to the mutual solubility of alumina and chromia (corundum phase), alumina possibly does not affect the Cr²⁺/Cr³⁺ ratio as much as silica does.

On the contrary, in the ternary system Cr₂O₃-CaO-SiO₂, there is a ternary compound 3CaO·Cr₂O₃·3SiO₂, which corresponds to the natural mineral uvarovite (Ca₃Cr₂Si₃O₁₂), which belongs to the garnet group. If chromium is present in the 3+ oxidized state (oxygen potential in the gas phase is sufficiently high), the liquid phase has a miscibility gap into two liquids: nearly pure silica and silica-rich melt with 27% wt. CaO and ~1% wt. Cr₂O₃.

However, as was noted for binary systems, the level of oxygen potential, the presence of metallic chromium, and slag basicity (CaO/SiO₂ ratio) have

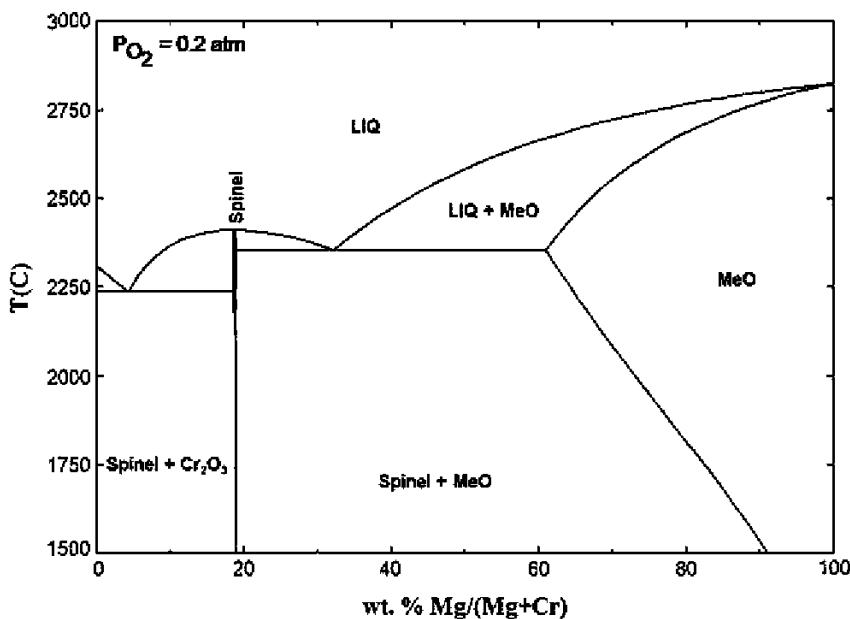


FIGURE 8.12 The $\text{MgO-Cr}_2\text{O}_3$ phase diagram at $P_{\text{O}_2} = 0.2 \text{ atm}$.

a strong effect on the chromium oxidation state, which might change from +2 (“ CrO ”) to +6 (CrO_3). Experimental studies (Villiers and Muan, 1992; Xiao and Holappa, 1993) have confirmed that for realistic conditions, more correct liquidus and solids equilibria could be achieved if this system is considered as a quaternary one: $\text{CaO-CrO-Cr}_2\text{O}_3-\text{SiO}_2$.

For the system $\text{Cr}_2\text{O}_3\text{-MgO-SiO}_2$, no ternary compounds have been reported, but a large miscibility gap was found. The major phases in this system are essentially chromia, MgO , and MgCr_2O_4 adjacent to the binary $\text{Cr}_2\text{O}_3\text{-SiO}_2$.

The substitution of different oxides has various effects on chromia activity (Xiao and Holappa, 1993). As might be expected, the substitution of CaO in slags by MgO lowers the activity of chromium oxides but does not significantly affect the $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratio. Minor additions of alumina increase the activity of chromium oxides, whereas higher amounts do not produce such effect. This shows that slags of ferrochromium processing might have rather different behavior if their composition varies during the process.

8.2 CHROMIUM RAW MATERIALS AND THEIR PROCESSING

8.2.1 Chromium Minerals Overview

Knowledge of the chromium ore minerals proper and their associated rocks-forming minerals is needed to explore new chromite fields and to predict the

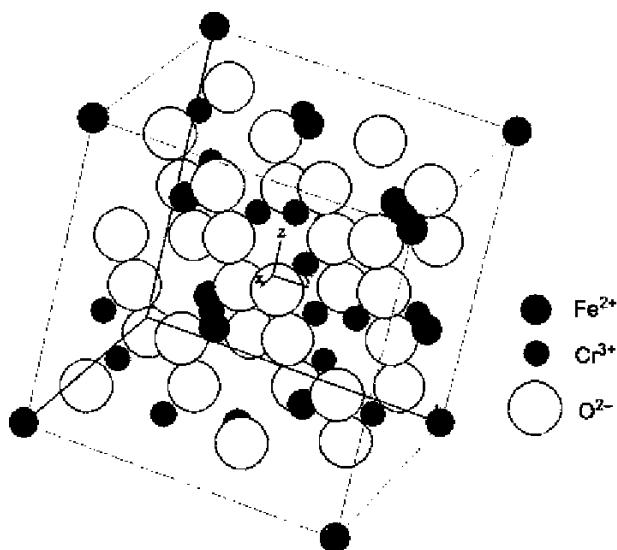


FIGURE 8.13 Crystal lattice of FeCr_2O_4 spinel structure (lattice parameter 0.88 nm).

efficiency of individual methods for the beneficiation of chromite ores. It is important also to know the physicochemical properties of individual mineral fractions of chromite ores and preparation of ore (or concentrates) for electric smelting, the fabrication of refractory materials, and the production of chemical compounds of chromium. The leading minerals of common chrome ores are chromium spinelides, which belong to the spinel group (natural spinel mineral MgAl_2O_4). All of these minerals crystallize in space group $Fd\bar{3}m$. The spinel group includes not only oxides, but also certain sulfides Cr_3S_4 , FeCr_2S_4 (daubreelite), and others. A unit cell of a spinel lattice contains 8 AB_2O_4 units (i.e., $\text{A}_8\text{B}_{16}\text{O}_{32}$). These 32 oxygen atoms constitute the closest cubic packing of 64 tetrahedral and 32 octahedral positions (Fig. 8.13). Out of 96 cation sites per unit cell, only 24 are included in this face-centered cubic cell.

A distinction is drawn between normal, inverse, and mixed structures of spinel. In a normal spinel, bivalent A^{2+} cations occupy tetrahedral sites and trivalent B^{3+} cations are located in octahedral sites. In inverse spinels, the octahedral A^{2+} cations occupy tetrahedral positions, and half of the B^{3+} cations (in the ideal case) are in octahedral sites. The normal and inverse arrangements of cations in natural spinels represent the ultimate limits of spinel structures when the spinel structural formula is presented in the form $(\text{B}_x\text{A}_{1-x})_{\text{tetr.}}(\text{A}_{x}\text{B}_{2-x})_{\text{oct}}\text{O}_4$. Normal spinel has $x = 0$ and inverse spinel has $x = 1$. Natural spinels are usually classified into four mineral species as series with Al^{3+} , Fe^{3+} , Cr^{3+} , and Ti^{4+} . All spinels with normal and inverse structures form solid solutions that are stable at certain temperatures and pressures (Lyakishev and Gasik, 1998).

TABLE 8.2 Approximate Composition of Chromium Spinelides from Different Countries*

Country	Content, wt. %				Ratios	
	Cr ₂ O ₃	Fe ₂ O ₃	MgO	Al ₂ O ₃	Cr/Fe	MgO/Al ₂ O ₃
Russia	30.54	27.38	24.16	17.92	1.12	1.35
Ukraine	37.15	19.16	18.06	20.78	1.94	0.87
Kazakhstan	60.765	1.845	15.695	8.32	32.93	1.89
Turkey	43.47	18.36	22.39	15.76	2.37	1.42
Greece	39.52	14.37	23.17	22.93	2.75	1.01
South Africa	46.63	11.97	22.75	18.63	3.90	1.22
India	55.2	16.7	14.1	14	3.31	1.01
Pakistan	49	14.37	22.29	14.33	3.41	1.56
Philippines	31.62	15.17	23.83	29.38	2.08	0.81
Canada	48.22	16.17	22.12	12.9	2.98	1.71
Cuba	28.46	13.57	24.29	33.68	2.1	0.72
Brazil	41.1	15.17	21.95	20.78	2.71	1.06

*There might be a large variation depending on the ore type (Karnouchov et al., 2001).

For example, chromites from certain ore deposits in Kazakhstan include chromium spinelides with a predominant content of $(\text{Mg}, \text{Fe})\text{Cr}_2\text{O}_4$, which contains some Al^{3+} in octahedral sites. The structural formula of chromium spinelides might be expressed as $(\text{Mg}_{5.44}\text{Fe}_{2.56})(\text{Cr}_{12.64}\text{Al}_{2.78}\text{Fe}_{0.58})\text{O}_{32}$. The composition ratios of chromium spinelides from different countries are shown in Table 8.2.

The following minerals might accompany chromium spinelides: chrome dioxide, chrome actinolite, chrome garnet (uvarovite $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$), kammererite $(\text{Mg}, \text{Fe}^{2+})_5\text{Al}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$, clinochlore $(\text{Mg}, \text{Fe}^{2+})_5\text{Al}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$, rhodochrome, serpentine (chrysotile $3\text{MgO}_2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), chrysotile asbestos, actinolite $\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH}, \text{F})_2$, magnetitecalcite $\text{MgCO}_3 \cdot \text{CaCO}_3$, antigorite $(\text{Mg}, \text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ olivine $(\text{A}, \text{B})_2\text{SiO}_4$, magnetite Fe_3O_4 , quartz, opal, pyrite FeS_2 , chalcopyrite CuFeS_2 , goethite FeOOH , limonite $(\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O})$, and hydrous ferruginous aluminosilicates. Chromite ores of certain deposits contain minerals of the platinum group (Ir, Ru, Pt, Pd, and Rh), especially in South Africa and Zimbabwe, often found as inclusions in chromite silicate matrix.

TABLE 8.3 Classification of Chromite Ores

Category	Type	% Cr ₂ O ₃	% SiO ₂
Commercial	High	58–62 50–58	0.3–3 3–8
	Medium	38–50	8–15
	Low	25–38	15–24
Noncommercial	Low	<25	>25

The mineral and gangue components have different magnetic susceptibilities, which makes it possible to use various magnetic separation methods. Typical values of magnetic susceptibility of chromium spinelides in Kazakhstan deposits are 35 to 70. Gangue minerals might have much higher values (asbestos with fine magnetite inclusions has 2260) or much lower values (chlorides 10 to 11, magnesite 2.5, calcite 5).

Depending on the concentration of chromium spinelides and overall composition of chromium ore (i.e., the content of Cr₂O₃), the deposits are subdivided by way of convention into commercial and noncommercial types (Table 8.3). High grades might be essentially processed without or with a little dressing procedure; other types require proper dressing technologies.

Chromium ores are also subdivided according to their physical state (strong, friable, pulverized, and silicified) and the chromites' grain size (coarse 7 to 15 mm, medium 1 to 7, and fine < 1 mm). So-called strong ores occupy ~80% of all chromite ores, friable ores occupy ~10%, and pulverized and silicified ores occupy 5% each (Lyakishev and Gasik, 1998).

The ores of certain sites might be enriched with or depleted in Cr₂O₃, as well as complementary SiO₂, Al₂O₃, MgO, Fe₂O₃, and CaO, even though they retained their original textural and structural characteristics. That makes it difficult to carry out selective mining and beneficiation. Therefore, it is essential to carry out the classification of chromium ores from commercial deposits, so as to be able to choose the most effective methods and parameters for dressing processes, to utilize ores and concentrates for smelting specific types of chromium ferroalloys, and to obtain chromium compounds and refractory materials.

8.2.2 Chromium Resources Overview

Reliable data on the explored world reserves of chromite ores are virtually absent, because different reviews and forecasts give widely different estimates of the reserves and production scale of chromite ore (Zhuchkov et al., 2010).

In some cases, where data are published they are not very compatible. In general, the republic of South Africa currently holds more than 70% (reserves 11 748 Mt, average 37% Cr₂O₃) of the world's known deposits and it is believed to be one of the world's leading suppliers. Neighboring Zimbabwe is the next major source with 25% (reserves 986 Mt, average 43.2% Cr₂O₃) of the known reserves. Other important chromite and ferrochromium producers are Kazakhstan (reserves 1316 Mt, average 50.2% Cr₂O₃), Turkey, Finland, and Brazil (reserves 72 Mt, average 22.3% Cr₂O₃). Other countries possessing explored commercial chromium ore reserves are Albania, Australia, Greece, India, Cuba, the Philippines, the United States, and Russia. Some deposits are being exploited in Armenia and Azerbaijan. The short summary of these chromite ore deposits is given below.

The main chromite resources of South Africa are associated with the Bushveld complex and the Witwatersrand system. The Bushveld complex represents deposits of chromite ores and platinoids situated in the Transvaal province in the territory of Rustenberg, Potgietersrust, Waterberg, and Leydenberg districts. The chromite deposit in the Bushveld complex is estimated at 2 billion tons.

The bulk of explored chromite reserves and their mining in South Africa are concentrated in the Rustenberg and Leydenberg districts. In the Republic of South Africa, chromite ores contain less Cr₂O₃ and have a lower Cr:Fe ratio, making them suitable mainly for the direct smelting of ferrochrome with a lower chromium content, the so-called charge chrome.

Chromites in Zimbabwe are mined mainly near the town of Selukwe. These Great Dyke range rocks are rich in iron and manganese, and also contain chromium, nickel, and other valuable metals. The metallurgical value of the chromites from the Great Dyke deposit varies from 40% to 50% Cr₂O₃ depending on the location. The major difference between Zimbabwe chromites and those of South Africa is that Zimbabwe ores have a higher Cr₂O₃ content and ratio Cr:Fe > 3:2. This makes them directly suitable for the smelting of commercial ferrochrome.

Turkey is one of the few countries that began mining and exporting high-grade chromites in the 1860s. The Guleman deposit chromites were the best in the world in terms of quality (52% Cr₂O₃). A large chromite ore deposit is situated near Eskisehir.

Finland occupies first place in Europe in terms of its amount of chromite, vanadium, and cobalt reserves; second place in terms of its titanium and nickel reserves; and third place in terms of its copper and pyrite reserves. The commercially exploitable chromite ore deposits are estimated at 165 million tons, although new deposits in the Kemi region have been recently examined. The mean Cr₂O₃ content is 26% with ratio of Cr:Fe = 1.5. Most chromite is used for the ferrochrome smelting factory at Tornio (this technology is somewhat unique, as liquid ferrochrome is used directly in steelmaking). The Cr₂O₃ content in the ore sent for concentration is 24% to 25% (Cr:Fe = 1.6 to 1.7) in the concentrates, the contents are 42% to 48% Cr₂O₃ and 2% to 5% SiO₂.

The commercial chromite ore deposits in the United States (reserves ~338 Mt) are located in Montana, Oregon, Alaska, and California. These are mostly low-grade ores (10% to 18% Cr₂O₃) and require dressing. Some deposits in Montana have ~25% Cr₂O₃, 7% SiO₂, and a ratio of Cr:Fe = 1.3 to 2.8. This ore is enriched to the concentrate grade of 42% to 44% Cr₂O₃, 17% Al₂O₃, and 3% to 4% SiO₂.

The ores in Russia (estimated reserves 486 Mt) contain mainly two types of chromite: medium (35% to 39% Cr₂O₃) and low-grade chromites (25% to 35% Cr₂O₃). Some chromites might have a higher content of Al₂O₃ (<20%). In the northern Ural region, chromites are of a high-chromium alumochromate type (Mg,Fe)(Cr,Al)₂O₄ (60% Cr₂O₃, 8.4% Al₂O₃, 12.84% FeO, and 5.52% Fe₂O₃). Chromite-bearing beds have also been discovered in Siberia and the Far East.

In Albania, rich deposits of chromium ore (48% Cr₂O₃ and 9% SiO₂) were discovered in the early 1930s near Lake Ohrid, in the vicinity of the town of Pogradec.

Australia has a large number of chromite fields, but they are low-grade types and, in most cases, require concentration processing. From 1930 to 1945, Australia was one of the major suppliers of chromite ores, producing 150,000 to 300,000 tons annually. The explored reserves of chromite ore in Australia have been estimated at 0.5 million tons.

Greek main deposits of chromite ore in Thessaly and the Chalcidice Peninsula have 40% Cr₂O₃, 12% FeO, 22% Al₂O₃, 18% MgO, and 5% SiO₂. Greece has one of Europe's largest chromite deposits at Skaumtsa.

A large chromite deposit in India is situated in Mysore, where reserves have been estimated at 1.32 million tons.

In Armenia, ore deposits in Shordzha having 22% to 33% Cr₂O₃ with the ratio MgO:Al₂O₃ ~1.4 have been reported.

Deposits of chromites in Azerbaijan (Geidar, Zandara) are medium grade (43% to 52% Cr₂O₃, 12% to 17% FeO, 5–6% SiO₂). There are, however, differences in alumina content from 10% to 17% (at chromia levels of 50% to 58%) to 23% Al₂O₃ with lower levels of Cr₂O₃ (<40%).

The chromite ores in Ukraine have a mean content of 30% Cr₂O₃, although there is a variation between different fields: medium grade (40% Cr₂O₃), low-grade (<25% Cr₂O₃), and noncommercial disseminated ones (6% to 15% Cr₂O₃). These chrome-spinelides belong to low-iron (Cr₂O₃:FeO = 2.4), high-chromium, medium-alumina varieties.

Some reserves in Greenland have been reported of order of 169 Mt with an average 21% Cr₂O₃ (Zhuchkov et al., 2010), but no specific details were given.

8.2.3 Chromium Ores and Chromites Processing

Chromite ores, as might many others, be mined by open-pit and underground methods. The share of underground mining varies between countries and deposits. The extracted ore is subjected to crushing and sorting (normally rich

TABLE 8.4 Typical General requirements for Chromite Ores

Customer Industry	Grain size, mm	% Cr ₂ O ₃	Others
Smelting of high-carbon FeCr	10–100	>49	
Smelting of low-carbon FeCr	0–10	>50	
Refractories (Cr-Mg bricks, etc.)	0.5–3 <0.5 – less 10%		<8% SiO ₂ , for high grades <3%
Chemistry (Cr compounds)	<0.5	>49	

ore containing more than 45% Cr₂O₃ is supplied to the processing plant, whereas lower-grades are subjected to different dressing procedures).

The main consumers of chromite ore are the ferroalloy, refractory, and chemical industries, which have different demands for the ore and the concentrates, both in terms of the impurity ingredients and in grain-size composition (Table 8.4).

A typical technological process of chromite ores enrichment includes a series of operations (Lyakishev and Gasik, 1998): screening of the input ore, slurry rinsing-off, and heavy media separation. The slurries formed are subjected to wet screening, dehydration, filtration, and drying. The major parameter, changing in these phases, is the SiO₂ concentration gradually changing to <7, 5, 3, and 1%. Because these low-silica concentrates are represented by finer fractions, it is important to prepare the product in lumpy forms (pellets, briquettes). It has been recommended that fine concentrate should be granulated and roasted (~1800°C).

The most common method is gravity concentration (heavy-media separation, screw separators, and concentration tables). Aside from the gravity method (in various modifications), flotation methods are used (separately or in combination with gravity methods), as well as concentration in a strong magnetic field. Magnetic concentration in a weak field is also used to extract magnetite from chromium ore before flotation or to extract it from chromium concentrate after flotation (Kurochkin, 1988; Lyakishev and Gasik, 1998). Wet high-gradient magnetic separation is usually thought to be the most promising method for improved performance. Chromite ore can be separated in a high-strength field, despite the presence of iron impurities. The choice of method depends on several factors, primarily the type of the gangue.

In some cases, separation and dressing methods are optimized to take into account other useful elements, such as PGM (platinum group metals) in South Africa, where noble metals extraction (besides chromium) is of high importance. Along with gravity-flotation and magnetic methods, hydrochemical (hydrometallurgical) technologies are being developed.

Besides these ore dressing methods, combined techniques are also possible, especially when the chromite quality is low. In India, low Cr:Fe ratio chromites are briquetted with coke and selectively reduced at 1250°C. Treated briquettes are crushed, ground, and leached, leading to the higher Cr:Fe ratio concentrates with chromium extraction exceeding 95%.

The authors have estimated that more than 75% of chromite ores are represented by fine fractions and the remaining share is represented by lumpy ores. Electric furnaces consume approximately two thirds of all mined chromite ore, and there the optimum operating conditions are achieved with large sorted chromite ore. For metallurgical processing of high-chromium concentrates, usually present in the finest forms, they have to be agglomerated. Although some successful experiments were made for smelting of ferrochromium in various metallurgical furnaces using fines, this technology has not yet been implemented on an industrial scale. For chromites agglomeration, three main methods are being exploited: sintering, palletizing, and briquetting.

Sintering technology originates from the similar method used for iron ores agglomeration. Many combinations of ores, carbon fuels, moisture content, and binders (bentonite) have been studied. An example of different versions of sinter charges is shown in Table 8.5. The addition of iron ore depends on the required Cr:Fe ratio, fines fractions, and chromite quality.

The pelletization of chromite fines and concentrates is usually based on mixing chromites, binder (bentonite), recycled material, and possibly coke fines and roasting at sufficiently high temperatures (1200° to 1300°C). It is known that roasting in air results in better pellet quality due to the oxidation of iron (2+ to 3+) taking the octahedral sites in spinel structure. A minor share of coke fines in the pellets gives the possibility of raising the temperature and gets more uniform temperature distribution inside the pellet. However, a better resistance to impact and abrasion was achieved in pellets with no fuel additions. During roasting, sulfur is removed from the pellets by 70% to 80% (due to oxidation of sulfides like pyrite). The remaining sulfur is of the sulfate type

TABLE 8.5 Example of the Charge Components for Chromites Sintering by Different Sources

Components	Russia (Ural)	India	Russia
Iron ore			15%–25%
Moisture	7.2%	10%	Not specified
Recycled material	33%	40%	
Coal	5%		Not specified
Coke dust		18%–20%	

TABLE 8.6 Some Examples of Chromite Pelletizing Technologies

Technology	A	B	C	D
Ore grain size	+150...300 mesh	Not specified	"Large"	Not specified
Water, %	12–14	Not specified	9	Not specified
Binder, %	bentonite 0.5–2	Caustic magnesite	Bentonite, filter cake	Lime 2–3, bauxite ore tails 4–5
Drying	150°C	380–400°C		187°C at 1.3 MPa
Roasting	700°–1000°C	Alternatively, 1700°C	1300°C	None

(magnesium and calcium sulfates). Some examples of pelletization technology parameters by different sources are shown in Table 8.6.

Briquetting as a method for agglomeration of fine fractions is widely used in ferrous and nonferrous metallurgy. Unlike sintering or pelletization, it is possible to make briquettes of single component (monobriquettes). In many cases, briquetting was reported to be commercially competitive with sintering or pelletization—the latter is associated with high capital investment, high cost of the grinding and roasting, demand for low SiO₂ content because of possible sintering of pellets when they are roasted in rotary kilns, and so on. The clear environmental advantage of briquettes versus lumpy ore is in the reduction of dust emissions by 1.5 to 2.5 times.

In developing a technology for briquetting of chromite ore, it is important not only to study the mineralogical and grain-size characteristics but also to make a proper choice of the type and quantity of the binder and the conditions for pressure and heat treatment of raw briquettes (Sen et al., 2010). It should be noted that it is very difficult to make recommendations about briquette quality with a particular charge and processing parameters, as well as whether they would be suited for effective smelting of ferrochrome in a submerged arc electric furnace (Pavlov et al., 2010). For example, briquettes in the furnace bath are also a current conductor, so extra coke in briquettes may lead to their premature destruction in the case of high current density. On the other hand, briquettes produced by this method are a good regulator of electric resistance in the charge.

Different compositions have been suggested for briquetting chromites using coal, tar resin, sulfite solution (lye), lime, and so on. One of the recommended briquetting methods is as follows (although it should be remembered that no defined remedy recipe exists for briquetting all types of chromite ores). The ore

of the 6 to 10-mm fraction is dried and mixed with hydrated lime to which mixture molasses is added at 35° to 40°C. The formed briquettes are 2 to 5 inches long, 1 to 2 inches thick, and 1.5 to 2.5 inches wide, and they are stored in piles; their strength increases slowly with holding, reaching maximum values (8 to 25 MPa) after 10 to 12 h. The briquettes retain their strength values even in humid conditions (for shipping and handling, >8 MPa is considered a sufficient limit). The exact mechanism behind the process of strengthening is not known, but some have speculated that it is related to calcium hydroxide carbonization or molasses transformations.

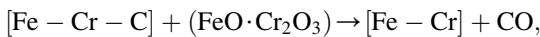
8.3 CHROMIUM FERROALLOYS TECHNOLOGY

The ISO 5448 standard has specified the composition ranges for both chromium and carbon. Ferrochromium is divided into three groups: high, medium, or low carbon. There are five major ranges of chromium content with averages of 50%, 60%, 70%, 80%, and 90% Cr with $\pm 5\%$ tolerances. The nominal composition of the high-carbon ferrochrome alloys is shown in Table 8.7. Typical high-carbon ferrochrome has 60% to 70% Cr, 6% to 8% C, and <5% Si (Chapter 9). Other commercial ferrochromium alloys are low-carbon (Table 8.8) and medium-carbon (Table 8.9) ferrochromium. Low-carbon grades of ferrochrome (<0.25% to 0.50% C) are mostly used to produce corrosion-resistant chromium-nickel and chromium (superferritic) steels. Explicit limitation of phosphorus content in low-carbon and medium-carbon FeCr is dictated by low phosphorus and sulfur demand in steels and difficulties of phosphorus removal from the steel melt bath after the addition of FeCr. All components of the charge are sources of phosphorus. Phosphorus of the charge materials is reduced also by chromium and practically completely transfers into ferrochrome.

Besides these bulk ferrochromium alloys (Daavittila et al., 2004), there are also specific grades of ferrosilicochrome (FeSiCr), ultra-low carbon FeCr, nitrided ferrochromium (FeCrN), and metallic chromium; their compositions and production technologies are described in other chapters.

8.3.1 Technology of Low-Carbon Ferrochrome

Low- and medium-carbon ferrochrome can be produced in several ways (Bobkova, 1991; Durrer and Volkert, 1972; Karnouhov et al., 2001; Lyakishev and Gasik, 1998). In some of them, the raw material is high-carbon ferrochromium, from which carbon has been removed via oxidation, either by chromite additions,



or by gaseous oxygen (converting),

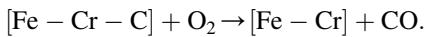


TABLE 8.7 Nominal Composition of High-Carbon FeCr Alloys*

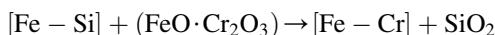
FeCr Grade	C, wt. %	Si, wt. %
FeCr...C50	4–6	<1.5
FeCr...C50LS		
FeCr...C50Si2		1.5–3
FeCr...C50Si2LS		
FeCr...C50Si4		3–5
FeCr...C50Si4LS		
FeCr...C50Si7		5–10
FeCr...C70	>6–8	<1.5
FeCr...C70LS		
FeCr...C70Si2		1.5–3
FeCr...C70Si2LS		
FeCr...C70Si4		3–5
FeCr...C70Si4LS		
FeCr...C70Si6		5–10
FeCr...C90	>8–10	<1.5
FeCr...C90LS		
FeCr...C90Si2		1.5–3
FeCr...C90Si2LS		
FeCr...C90Si4		3–5
FeCr...C90Si4LS		

*Note that “...” is replaced by the respective average chromium content. All grades have maximal sulfur content of 0.10% S except LS grade (“low sulfur”) for 0.05% S.

Low-carbon FeCr might be also produced by oxidation of FeSiCr melt with chromite:



as well as reduction of chromite with silicon (FeSi):



The latter method is similar to the previous process and historically it was developed first (Lyakishev and Gasik, 1998), but the chromium content therein

TABLE 8.8 Nominal Composition of Low-Carbon Ferrochromium Alloys*

Grade	C wt. %	Cr wt.%	P, wt. % max
FeCr...C01P	<0.015	45–75, 75–95 [†]	0.02, [†] 0.03
FeCr...C01			0.05
FeCr...C03P	0.015–0.03	45–75, 75–95 [†]	0.02, [†] 0.03
FeCr...C03			0.05
FeCr...C05P	0.03–0.05	45–75, 75–95 [†]	0.02, [†] 0.03
FeCr...C05			0.05
FeCr...C1P	0.05–0.1	45–75	0.03
FeCr...C1			0.05
FeCr...C2P	0.1–0.25	45–75	0.03
FeCr...C2			0.05

*All grades have <1.5% Si, <0.03% S, and <0.15% N.

[†]Maximal phosphorus content of 0.02% marked is for the highest chromium content (in the 75% to 95% Cr range).

TABLE 8.9 Nominal Composition of Medium-Carbon Ferrochromium Alloys*

Grade	C wt. %	Cr wt.%	P, wt. % max
FeCr...C10	0.5–1	45–75	0.05
FeCr...C10LP			0.03
FeCr...C20	1–2	45–95	0.05
FeCr...C20LP			0.03
FeCr...C40	2–4	45–95	0.05
FeCr...C40LP			0.03

*All grades have <1.5% Si and <0.03% S (except <0.05% S for non-LP grades).

is limited. It is also possible to combine several methods, such as reduction of quartz in the presence of high-carbon FeCr with production of FeSiCr, from which silicon is removed by adding chromite (the resulting slag has a high chromia content and is recycled back to the high-carbon FeCr smelting) (Karnouhov et al., 2001).

Low-carbon ferrochrome is also produced by aluminum reduction, which is discussed in Section 8.4 in more detail. However, in any of these methods, reduction products (either SiO_2 or Al_2O_3) dissolve in the slag, reducing the activity of chromium oxide and making further reduction more difficult. To compensate, increasing slag acidity lime must be added and thus both methods require a substantial amount of flux.

The aluminum reduction process might supply all the heat needed for the reactions exothermally and therefore might be carried out of the furnace, requiring no external heating. In practice, however, some heating is used to reduce the consumption of aluminum powder. Silicon reduction can be carried out exclusively in an electric furnace or by first smelting FeSiCr and mixing it with chromite melts in a ladle.

Reduction by silicon proceeds in the presence of lime (CaO), resulting in a decrease of silicon content in the metal melt (starting FeSiCr) and an increase of chromium in the metal and SiO_2 in the slag. As was mentioned in the description of the Cr_2O_3 -“ CrO ”- SiO_2 - CaO system, the ratio $\text{Cr}^{2+}/\text{Cr}^{3+}$ is very dependent on the slag basicity. Experimental data with different slag compositions (Durrer and Volkert, 1972; Lyakishev and Gasik, 1998) show that the Cr^{2+} fraction has a clear trend to drop at high basicity values (Fig. 8.14). Besides that, the distribution of Cr^{2+} in the volume of the slag is not uniform. In the surface layer of slag, the fraction of Cr^{2+} is below 20% to 25%, depending on the total chromium content in the slag, whereas close to the slag–metal interphase boundary it increases to 40% to 70%.

Therefore, during the process the ratio $\text{Cr}^{2+}/\text{Cr}^{3+}$, and activities of silica, MgO , and CaO in the chromite–lime slag change continuously, which is also

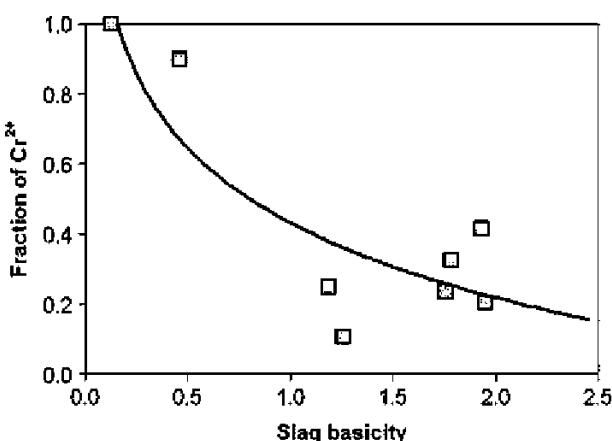


FIGURE 8.14 Molar fraction ratio $\text{CrO}/(\text{CrO} + 2\text{Cr}_2\text{O}_3)$ versus slag basicity expressed as $(\text{CaO} + \text{CrO} + \text{MgO} + \text{FeO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3)$.

affected by oxygen from the furnace environment (the process is very sensitive to the oxidation-reduction potential of the gas phase). In the metal phase, activities of chromium, silicon, and iron also vary. This makes thermodynamic analysis of the reactions very challenging. Furthermore, the limiting silicon content (<1.5%) and the requirement of the highest possible chromium extraction set additional constraints in defining the optimal process conditions. As the reactions of Cr_2O_3 with dissolved silicon are exothermic, increasing process temperature leads to higher silicon content in the FeCr melt.

Process slags contain a substantial amount of MgO besides added lime. Excess lime dilutes slag, increases viscosity, and slows reaction kinetics in general. Excess MgO decreases possibilities for a silicon reaction with chromite, and therefore its content should be limited to 12% to 14% wt.

In practice, the conditions for producing low-carbon ferrochrome in electric arc furnaces are determined experimentally by varying the method of FeSiCr, chromite ore, and lime loading; charge composition; heating and electrical conditions; as well as the quality of refractories and electrodes. In the electric-furnace method of producing low-carbon ferrochrome by silicon reduction, there is a correlation between silicon content in the ferrochrome and Cr_2O_3 in the slag. In the conditions of industrial production of low-carbon ferrochrome, slags with lower basicity (<1.8), high-quality lime, and FeSiCr have provided the best results. Among these, the use of high-quality graphitized electrodes is an important factor (if the electrode quality is lacking, carbon particles might drop off into the slag melt). When the slag basicity is high, carbon may react with calcium and chromium oxides, forming their carbides, and these are a source of increased carbon in the ferrochrome. This sometimes justifies the production of ferrochrome with <0.03% C by mixing a slag melt with liquid or solid FeSiCr outside the electric arc furnace, despite the fact that it makes the processing organization more complex.

8.3.1.1 Furnace Method

The quality of the FeCr and the features of the whole process are very much determined by the method of loading the charge components into the furnace and the conditions used for the decision of the tapping moment. Different options have been utilized, such as: a) loading all components at once, b) loading all components except FeSiCr (for which the second part is added later), c) loading a small amount of FeSiCr to establish an electric load, and then adding other charge components and finally the rest of the FeSiCr. The following procedure has been considered the most appropriate (Table 8.10).

The processing of low-carbon FeCr is usually carried out in small furnaces (5 MVA) lined by magnesite (MgO) bricks. The furnace is loaded with the first part chromite ore, lime, and the first part of FeSiCr. After melting, the second part of FeSiCr, chromite ore, and lime is loaded, the melting is finished, and the metal and slag are tapped. The appropriateness of heat-tapping was earlier

TABLE 8.10 Comparison of Technological Operations of Smelting of Low-Carbon Ferrochrome

Ferrochrome Grade	FeCr...C2(P)	FeCr...C05(P)
Charge (1st/2nd period), kg		
Chromite ore	5200–5800/5200–5800	5600–5800/5600–5800
FeSiCr	1700–1900/1700–1900	2000–2400/1200–1400
Lime	4200–4700/4200–4700	3600–4000/3600–4400
First period:		
FeSiCr loading	700–1000 kg first	700 kg first, then 1300–1400 kg after ore–lime addition by 200–250 kg batches
Chromite ore–lime	With remaining FeSiCr	After first FeSiCr
Tapping	Slag only	None
Second period:		
FeSiCr loading	700–1000 kg first	400–500 kg first, then 800–900 kg after ore–lime addition
Chromite ore–lime	With remaining FeSiCr	With remaining FeSiCr
Tapping	Slag and metal	Slag (1 and 2 period) and metal
Additional operations	+25–50 kg FeSi at the end of each period	
Slag basicity	1.7–1.9	~1.7
% Cr ₂ O ₃	4–5	5–6
% CaO	48–51	45–46

judged according to the amount of electrical energy fed into the furnace, but more recently the direct measurement of silicon in the metal melt has been considered a more reliable control.

8.3.1.2 Off-Furnace Technology (Mixing Method)

For ferrochromium with the least carbon content, furnace graphitized electrodes have been identified as a major source of carbon, accounting for ~40% of

all carbon input. In this case, the chromite ore–lime melt is made in the furnace without reduction, and it is mixed with FeSiCr in a ladle, outside the furnace (the mixing method, also known as the Perrin process). During the melting of the chromite ore and lime mixture, the oxidation potential is high (no metal formed) and thus carbon content in the slag is low. During mixing, there are no graphitized electrodes and a large amount of heat is released due to exothermic reactions of chromium and iron oxides with silicon and of interaction of CaO with SiO₂. The heat release is high enough to allow the use of solid FeSiCr along with liquid FeSiCr.

The mixing process is highly turbulent, kinetically fast (at the beginning of the mixing stage), and efficient enough to remove silicon from the FeCr melt. The slag might be used in several ladles to enhance refining of the FeCr from silicon; however, the main objective of the mixing method is essentially low-carbon FeCr processing. The disadvantages of the mixing method are increased nitrogen content in FeCr and some more challenges to control chromium-rich emissions (dust, fumes, gases).

The charge materials used to produce low-carbon FeCr are chromite ore, lime, and FeSiCr. The starting charge materials have to be classified depending on phosphorus concentration, as phosphorus content affects the quality of ferrochrome. Besides these main charge materials, the returns from the gas cleaning units (cyclones) with 25% to 40% Cr₂O₃ are also used as charge components. FeSiCr is used in a liquid (melt) or solid (granules) form and its typical composition is 48% to 51% Si and 28% to 30% Cr, with the balance composed of Fe and impurities. The main requirement to FeSiCr is that phosphorus content should not exceed 0.02% wt.

Chromite ore and lime are fused in small electric furnaces (~5 MVA) lined with MgO bricks, and fed through graphitized electrodes. The ratio of chromite ore to lime is roughly 1:0.8, and the resulting melt has about 27% to 30% Cr₂O₃ and 40% to 45% CaO. To accelerate melt formation, a small fraction of FeSiCr is added to form silica for the purpose of reducing the liquidus temperature.

The chromite ore–lime melt is poured into a ladle (5 to 6 m³) with a magnesite lining. To decrease heat losses, the melt in the ladle is covered with slag from previous heats. The ladle with the melt is weighed and the amount of FeSiCr additions is calculated depending also on the content of Cr₂O₃ in the melt. The FeSiCr is poured into the ladle while it is on the scales. The pouring rate is adjusted to the rate of reduction processes in the ladle (~200 kg FeSiCr per minute). At the end of pouring, the contents of the reactor ladle are transferred to another ladle and then back to the first ladle. The number of pourings between ladles (up to six times) is determined by the rate of refining ferrochrome from silicon.

Another example of the smelting hardware in the Tchelyabinsk plant (Russia) includes a closed submerged arc furnace, 33 MVA (bath inner diameter 8.8 m, depth 3.5 m, electrodes 1500 mm) for smelting of FeSiCr and 16.5 MVA (bath inner diameter 4 m, depth 2.35 m, electrodes 500 mm) for

chromite ore–lime melt preparations. For the latter process, the chromite and limestone are preroasted in rotary kilns at 1100°C, and this hot charge is fed directly into the furnace. The chromite ore–lime melt is tapped at ~1900°C into a magnesite-lined ladle and is mixed with liquid FeSiCr in a 20 m³ ladle. The cross section of the chromite–lime melting and mixing plant is shown in Figure 8.15.

The specific consumption of raw charge materials for the production of 1 ton of low-carbon ferrochrome by mixing is 1750 kg of chromite ore (basis 50% Cr₂O₃), 570 kg of FeSiCr with 48% Si, 1370 kg lime, and 18 kg of electrodes. Electricity consumption varies, but the chromium extraction efficiency is ~80%.

The exothermal reactions of chromium reduction by silicon give about one fourth of total heat input in the balance, which is enough for raising the temperature of the process and melting the solid charge.

A version of the mixing process operation involves reaction in a converter with argon blowing (Lyakishev and Gasik, 1998). Here chromite–lime melt was poured into a converter, followed by the addition of FeSiCr and subsequent agitation by argon. To control melt temperature and to avoid overheating, a mixture of chromite and lime was added. The length of the converting cycle was from 10 to 30 minutes. The low-carbon FeCr obtained in this way had 0.02% C, 62.2% Cr, and 0.03% P with residual chromia content in the slag of 3% to 4%; however, the extraction of chromium was about 80% (i.e., not very different from the conventional mixing process without argon blowing).

Low-carbon ferrochrome is cast into iron molds into ingots with a thickness < 80 mm if no degassing is applied. Ferrochrome produced by mixing contains a substantial amount of dissolved gases (up to 30 cm³ per 100 g).

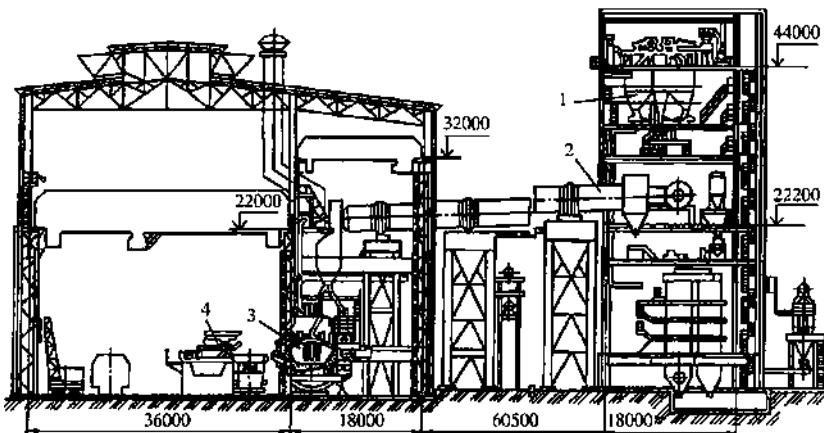


FIGURE 8.15 Cross section of the plant for melting of the chromite ore–lime melt and mixing process (dimensions in mm) using a preheated charge. 1, dosing equipment; 2, rotary kiln; 3, electric furnace; 4, ladles for mixing of ore–lime melt and FeSiCr.

Upon solidification, excess gases form cavities and small bubbles. This has a negative effect on ingots crushing (more fines and dust) as well as steelmaking (less dense FeCr lumps do not sink well enough in the steel bath, leading to excess chromium losses). Therefore, it is a common practice to carry out degassing of FeCr before its casting by subjecting the ladle to a vacuum treatment (<10 min). After that, the slag pots are filled first to 70% of their volume with liquid slag and the rest of the slag from the ladle is poured into separate slag ladles. After few minutes, when the slag lining has been formed, the FeCr melt is poured into ingots with a thickness of less than 150 mm.

The mixing method also allows production of master alloys that contain elements such as molybdenum, tungsten, and manganese, which are easier to reduce than chromium.

Similar to the furnace method, mixing might be carried out in different stages. For example, extra FeSiCr might be poured first into the oxide melt to get FeCr with a high silicon content. This melt is treated with extra oxide melt, reducing silicon content down to the required values but leaving slag with a high Cr₂O₃ content, which in turn is repeatedly treated with excess FeSiCr. Also, the mixing of different heats is being practiced.

Residual slag from low-carbon FeCr smelting has high basicity (CaO:SiO₂ > 1.6). This creates favorable conditions for the formation of calcium orthosilicate 2CaO·SiO₂ as the main mineral component of the slag. The polymorphic transformation of calcium orthosilicate upon cooling with more than 12% volume increase leads to slag self-crushing and excessive dusting (particle sizes <0.1 mm). To combat this problem, MgO and some other oxides (B₂O₃, BaO) are used to stabilize the mineral composition of the slag. Slags with basicity of 0.9 to 1.2 and 15% to 18% MgO have a stony structure, are characterized by high strength, and do not disintegrate with prolonged storage (Bobkova, 1991). However, separation of these slags from metal is more difficult and requires additional crushing and separation steps. Nonstabilized slags have sometimes been used as a calcium orthosilicate source (in molding sands binding, construction mixes, etc.). For example, there have been positive outcomes to the use of low-carbon FeCr dump slags in agriculture (fertilizing, increasing soil basicity), road construction (filling material), cement processing, and colored and special glass manufacturing, and as a pigment in paints (Karnouhov et al., 2001).

8.3.2 Technology of Medium-Carbon Ferrochrome

Medium-carbon ferrochrome is also a product of interest in the foundry industry and in steelmaking plants where refining capacity is limited but low silicon content is desired. Most of the medium-carbon FeCr is produced by the oxygen-converter method. It is based on carbon removal from liquid high-carbon ferrochrome (8% to 9% C, 0.3% to 0.5% Si, 0.04% P) with gaseous oxygen blowing (Karnouhov et al., 2001; Lyakishev and Gasik, 1998).

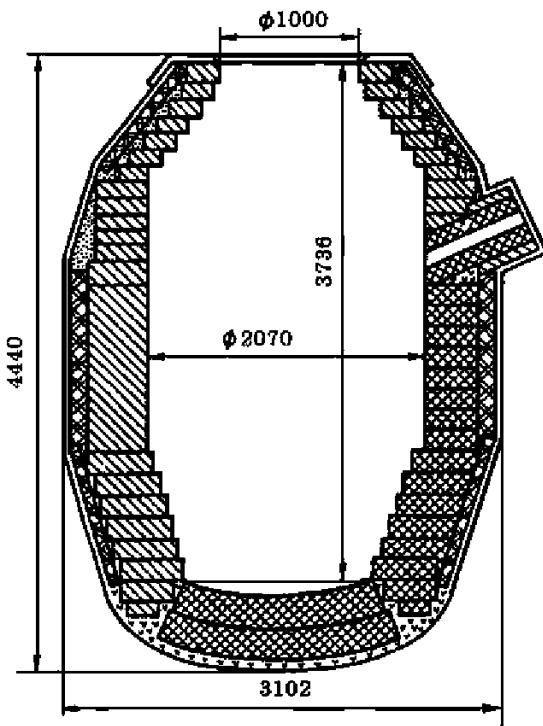


FIGURE 8.16 Dimensions (mm) of the top-blown converter for the production of medium-carbon ferrochrome.

A typical converter is the top-blown type and it has capacity of 15 tons of liquid FeCr (Fig. 8.16). The converter is lined with chromium–magnesite and periclase (MgO).

The idea of the carbon removal from the liquid FeCr is based on carbon oxidation during oxygen blowing. As FeCr has a limited amount of silicon, silicon oxidation cannot be used as a heat source (furthermore, the formation of silica would have negatively affected the lifetime and stability of the lining). The melt temperature at the beginning of the process is not sufficient for carbon oxidation, and it only starts to proceed together with chromium oxidation after some time. Carbon and chromium oxidize simultaneously, but at higher temperatures chromium oxide from the slag phase starts to react with carbon in the metal phase, releasing free chromium and CO (these reactions are endothermic and require higher temperatures). The ratio Cr:C in the melt during oxygen blowing is a function of melt temperature and might be approximated by $\log (\text{Cr/C}) = -10850/T + 7.12$ (Gasik et al., 2009; Lyakishev and Gasik, 1998). Increasing temperature by 200 K results in an equilibrium residual carbon decrease from 3.1% (1873 K) to 0.92% C at 2073 K. To reach high

temperatures, aluminum-rich scrap ~5 to 8 kg/ton is sometimes used (aluminum oxidation is highly exothermal).

The refining process is carried out by pouring 7 to 11 tons of liquid high-carbon FeCr into a converter (>60% Cr, <1% Si, <0.05% P— carbon content is not limited). For every ton of FeCr, 80 to 100 m³ oxygen is required. At the end of blowing, 600 to 800 kg of medium-carbon FeCr returns are added to cool down the melt; 15 to 20 kg of FeSiCr is also added to enhance slag reduction and decrease its viscosity. Tapping of metal and slag is carried into metal mold. For 1 ton of ready medium-carbon FeCr, about 1230 to 1260 kg of high-carbon FeCr is required at a chromium extraction efficiency of 80% to 82%.

8.3.3 Technology of Ferrosilicochrome (FeSiCr)

Ferrosilicochrome (FeSiCr) is an alloy of the multicomponent system Fe-Cr-Si with carbon, phosphorus, and sulfur as main impurities. The FeSiCr alloy is produced for two purposes: direct use in steelmaking (steel bath killing and alloying with chromium and silicon) and as a reductant in processing of low-carbon FeCr as described previously. The typical compositions of FeSiCr alloy are shown in **Table 8.11** (there are several national standards and plant norms for FeSiCr grades, especially when it is used in house for low-carbon FeCr production only).

The carbon content in FeSiCr for the production of medium-carbon ferrochrome is not regulated, as it is determined by the concentration of silicon in the alloy. Obtaining the alloy with the highest silicon content (>45%) and lowest carbon content (<0.05% C) is a challenging engineering operation. This alloy is intended for the production of low-carbon ferrochrome with <0.07% C (by the furnace method) and <0.03% C (by the mixing method with FeSiCr).

FeSiCr can be produced by a slag-less or slag (flux) process. In the first case, the reduction of silicon by carbon (coke) from quartzite charge proceeds in the presence of high-carbon FeCr (i.e., here chromium is not reduced, only silicon).

TABLE 8.11 Chemical Composition Requirements for Typical FeSiCr Alloy Grades

Grade	Si, wt.%	Cr, wt. % min	C, wt. %	P, wt. % max	S, wt. % max
FeCrSi13	10–16	55	6	0.04	0.03
FeCrSi20	16–23	48	4.5	0.04	0.02
FeCrSi26	23–30	45	3	0.03	0.02
FeCrSi33	30–37	40	0.9	0.03	0.02
FeCrSi40	37–45	35	0.2	0.03	0.02
FeCrSi48	>45	28	0.1	0.03	0.02

In the second method, chromite ore is added so both chromium and silicon are reduced simultaneously by carbon.

The slag-less process uses coke, quartzite, and high-carbon FeCr. Silicon is reduced by carbon from both coke and FeCr, and chemically the process is close to smelting of ferrosilicon with 45% to 65% Si. Silicon dissolves in the Fe-Cr-C melt and its activity is significantly lower than for FeSi alloy processing. As silicon reduction proceeds through several intermediate stages, gaseous SiO and solid SiC form. The concentration of SiO in the gas phase is high, 30 to 40 vol %, and might lead to losses of silicon and distortions of the closed arc furnace operations. The formation of very fine SiC particles is undesirable; therefore, the melt is soaked in a ladle for an hour to allow SiC to float to the top of the melt. Nevertheless, the quality of the FeSiCr alloy by this method is lower than it is with the flux process.

In the single stage slag (flux) method, chromite ore is charged instead of high-carbon FeCr. This leads to a complex mechanism of melt and slag formation. Their properties have an important role in the production of alloys with lower carbon content. The slag may have different silica content and various MgO:Al₂O₃ ratios, depending on the quality and composition of raw chromite ore. It has been recommended that the ratio MgO:Al₂O₃ should be raised if silica contents increase (~1 for 45%SiO₂ and ~1.2 for 50% SiO₂).

An example of the submerged arc furnace of 33 MVA is shown in Figure 8.17. This furnace has a water-cooled shell, a carbon bricks lining, and self-backed electrodes of 1500 mm diameter. An electric circuit includes a capacitor battery with 12 MVAR power per current phase.

It is necessary for every furnace to maintain a proper height of carbon lining. Specific recommendations depend on the type of ferroalloy being produced. If the height of carbon brick walls is too high, a slag–carbide “false bottom” buildup is formed due to the excess availability of carbon. In such cases, removal of additional upper carbon blocks allows FeSiCr production with improved indicators.

The slag-less process of FeSiCr smelting is performed in such furnaces using a charge of high-carbon FeCr, quartzite, and coke. Quartzite (20 to 80 mm) is required to ensure low water content and porosity, as well as high thermal and cracking resistance. Coke (5 to 25 mm) is supplied at some surplus (<5%). Table 8.12 lists the normalized charge materials expenditure (per 1 ton of FeSiCr) with different levels of silicon content for slag-less and slag processes.

The standard operating current of the furnace (see Fig. 8.17) is 90 to 100 kA and the power factor $\cos(\phi)=0.90$ to 0.95. With these conditions, the temperature of off-gases ranges from 550° to 750°C, which reflects normal furnace operation. In the case of deviations, gas temperature might rise to 1300°C, and this is an indicator of abnormal operation requiring operator intervention and parameters adjustment. The composition of gas emerging from the electrodes zone is 10% to 12% N₂, 5% to 7% H₂O, 4% to 5% CO₂, balance CO, and impurities. In abnormal cases where the temperature is very high, the

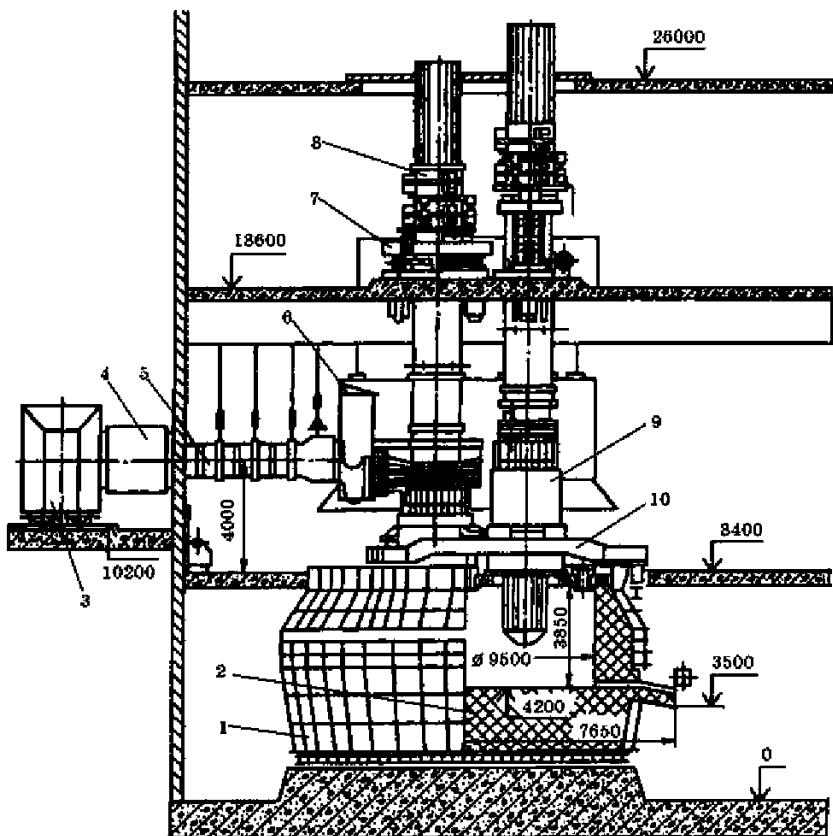


FIGURE 8.17 Submerged arc furnace of 33 MVA power for smelting ferrosilicochrome. 1, shell; 2, lining; 3, power transformer; 4, short net compensator; 5, short net; 6, screens; 7, hydraulic lift; 8, electrodes control and bypass mechanism; 9, electrodes holder; 10, furnace cover.

furnace operation is also disrupted by sublimes, forming alternating black/white layer deposits. Black layers are a combination of graphite (~16%), MgO (~40%), and SiO₂ (~40%); white layers are mixtures of oxides (~42% MgO, 23% SiO₂) and carbide (30% SiC). A high MgO content possibly originates from the oxidation of magnesium vapors given off from the reduction of magnesia. Sublimes have no MgO in the case of a slag-free process.

Slag-less FeSiCr smelting is a continuous process when the products are tapped every 1.5 to 2 h. The temperature of the liquid alloy at tapping is 1850° to 1950°C, dropping down to ~1600°C in the filled ladle. This temperature is much higher than that of the liquidus of the alloy (1320° to 1340°C) and such overheating is needed for soaking the alloy in the ladle for about an hour to allow formation, coagulation, and floating up of SiC inclusions (the carbon-saturated Fe-Si-Cr melt is in equilibrium only with silicon carbide). SiC inclusions have

TABLE 8.12 Charge Materials for Slag-Free (Top Rows) and Slag (Bottom Rows) Processes

Charge Materials, kg/t FeSiCr	Si, % wt.				
	13	23	33	43	50
Quartzite	298	520	742	965	1121
	634	881	1134	1323	1464
Chromite ore	not used				
	1908	1600	1420	1145	923
Coke	117	220	312	424	308
	543	575	625	678	712
High-carbon FeCr	1089	911	803	648	525
	not used				
Iron (steel) chips	8	41	62	93	115
	30	82	84	105	116

different origins, primarily as the result of SiO_2 reduction by carbon from the melt and secondarily as the result of the decreased solubility of carbon in liquid FeSiCr. There might also be external inclusions due to slag entrapping. Whereas these inclusions are the same for SiC compositions, the degree of their removal from the melt is different as they have a variety of particle sizes.

The duration of soaking in the ladle could be extended by preheating the ladle lining and by insulating the melt surface with a layer of high-basicity ferrochrome slag.

After the holding, FeSiCr alloy is cast into ingots or granulated by spraying the liquid alloy with a water jet. In the process granulating the alloy, the slag and SiC inclusions are washed off.

The slag amount in this process is 3% to 6% of the metal weight. The chemical composition of the slag varies significantly, due not only to furnace operation but also to chromite composition and the quality of other charge materials. Examples of FeSiCr process slag composition from three different plants are shown in Table 8.13. The “normal” slag composition is defined by SiC content that should not exceed 8% wt. The differences in the compositions shown are due to many factors. For example, some slags with a high content of BaO result from the use of quartzite in the Baikal deposit, which contains 0.2% to 1% BaSO_4 . Higher alumina (or a lower $\text{MgO}/\text{Al}_2\text{O}_3$ ratio) in the slag was achieved by adding bauxite or using chromite ore with $\text{MgO}/\text{Al}_2\text{O}_3 \sim 1$. Some

TABLE 8.13 Examples of Slag Compositions from FeSiCr Smelting*

Plant/Furnace	SiO ₂	Al ₂ O ₃	CaO	MgO	BaO	SiC	Cr ₂ O ₃
I	17–27	21–45	11–33	1.5–6.5	9–12	1–27	Not analyzed
II	36–51	14–28	2–18	2–8	—	7–70	0.5–6
III	26–32	17–25	12–20	1–2	12–20	8–11	2–6
IV	41–43	23–24	0.5–6	20–25	—	3–5	0.5–2

*Impurities not shown are mostly FeO (<4%).

furnaces operate with the addition of lumpy pegmatite rock (74% SiO₂, 13% Al₂O₃, 1.8% CaO, 10% (Na₂O + K₂O) and chromite ore with <20% MgO. The presence of alkalis decreases the viscosity of slags and improves the separation of metallic shots and SiC, leading to a higher alloy yield.

The mineral composition of the slags is governed by anorthite CaO·Al₂O₃·2SiO₂, gehlenite 2CaO·SiO₂·Al₂O₃, spinel MgAl₂O₄, and corundum Al₂O₃. Barium oxide (when present) tends to form celsiane BaO·Al₂O₃·SiO₂ and barium hexa-aluminate BaO·6Al₂O₃. Celsiane might also incorporate alkalis. The practical experience of ferroalloy plants indicates that FeSiCr slag containing inclusions of alloy and SiC should be utilized in the charge for producing high-carbon ferrochrome. The productivity of a 33 MVA furnace (see Fig. 8.17) with an operating active power of 28 to 30 MW is 120 to 130 ton FeSiCr per day.

8.3.4 Technology of Ultra-Low-Carbon FeCr

In some cases, the composition of standard low-carbon FeCr is not satisfactory for processing of special alloys and steels with an ultra-low carbon, hydrogen, and nitrogen content. Low-carbon FeCr with <0.03% C still has a too-high nitrogen content, significantly reducing the corrosion stability of Cr-Ni-Mo stainless steels, even when carbon in the steel does not exceed 0.015%.

A method has been developed to remove these impurities and oxide inclusions by subjecting solid FeCr lumps to a high-temperature treatment in a vacuum (Gasik and Polyakov, 1990; Lyakishev and Gasik, 1998). This method has been patented in many countries and has received widespread recognition, allowing production of FeCr with <0.015% C and <0.025% N. The principle of the method lies in solid-phase decarburization and the degassing of FeCr lumps with a starting carbon content of 0.10% to 0.15% in a vacuum (residual pressure 1.3 to 13 Pa) at 1350° to 1450°C in three-chambered resistance furnaces (Figs. 8.18 and 8.19). During the treatment carbon content drops from 0.10% to 0.02% C and nitrogen from 0.06% – 0.07% to <0.02% N. The ferrochrome

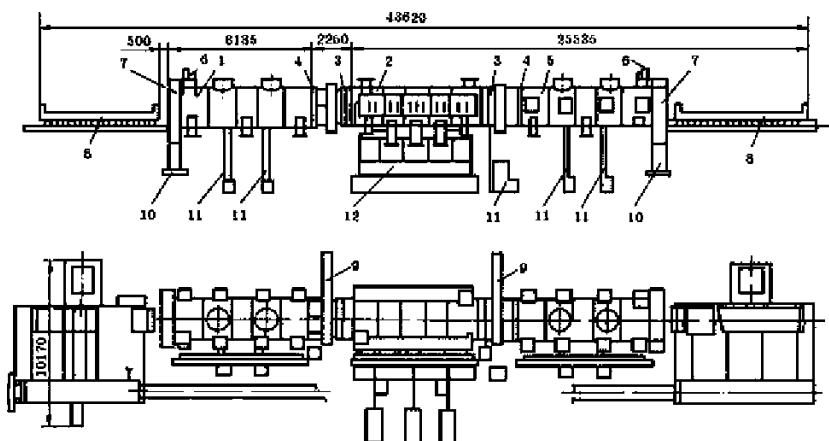


FIGURE 8.18 Vacuum furnace layout for processing ultra-low-carbon ferrochromium by the method designed at the Dnipropetrovsk Metallurgical Institute. 1, FeCr cooling chamber; 2, isothermal soaking chamber; 3, vacuum gates; 4, compensators; 5, preheating chamber; 6, cover lift; 7, cover; 8, carrier; 9, vacuum shields; 10, support; 11, low-vacuum pumps; 12, acceleration pumps.

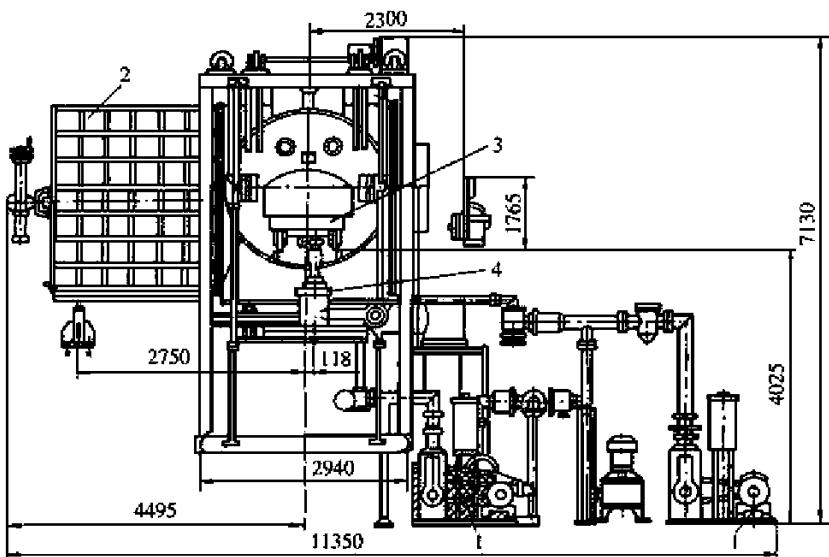


FIGURE 8.19 Cross section of the vacuum furnace for ultra-low-carbon FeCr processing (see Fig. 8.18). 1, pumps; 2, vacuum slag; 3, carrier; 4, carrier moving mechanism.

degassed by this process is also characterized by low concentrations of hydrogen ($\leq 7 \cdot 10^{-4}$ %), oxygen (≤ 0.04 %), and nonmetallic inclusions.

This furnace of 1.5 MW power operates at 1050°C in the first chamber and 1350° to 1450°C in the second chamber (the third chamber is used for cooling). The entire cycle time is 24 h. Carbon, nitrogen, hydrogen, and oxygen are removed by the diffusion mechanism. Oxide inclusions might be partially reduced in the vacuum. This method is only useful for solid-state FeCr refining, as liquid ferrochromium would have too many losses of chromium with vapors.

8.3.5 Technology of Nitrided Ferrochromium (FeCrN)

In the case of low-, medium-, or high-carbon ferrochromium, nitrogen content is usually limited (Tables 8.7 to 8.9). However, when making Cr-Ni-Mn and Cr-Mn stainless steels as well as some other special grades, part of the nickel is replaced by nitrogen, which stabilizes the austenite structure if properly dissolved in the FCC phase. It also improves some physical and mechanical properties of steels. The input of nitrogen into liquid steel from the gas phase is difficult and uneven, so the best way is to use nitrided ferroalloys (FeMn, FeCr, FeV), which might have up to about 10% wt. nitrogen. According to the method of nitrogen introduction in the ferroalloy, it might be classified as “molten” (nitriding proceeds in the liquid state) or “sintered” (nitriding proceeds in the solid state, e.g., by treatment of the alloy powder). The typical composition of these FeCrN alloys is shown in Table 8.14. On request, the alloy with a carbon content below 0.03% to 0.06% wt. C, phosphorus below 0.02%, silicon < 1%, and sulfur < 0.02% might be supplied.

The saturation of molten FeCr by nitrogen is performed while liquid low-carbon ferrochrome is soaked in a nitrogen atmosphere, traditionally in induction furnaces. Nitrogen dissolution in liquid FeCr is an exothermic process, and the solubility of nitrogen decreases with increasing temperature. Other elements also affect nitrogen solubility, such as the following:

1. Carbon decreases nitrogen solubility; in the Fe-70%Cr melt, solubility is described as $\log(\%) = 0.48 + 0.105(\%)$ at 1 atm and 1873 K.

TABLE 8.14 Nominal Composition of Nitrided FeCr, wt. %*

Grade	Cr	C	Si	P	N	S
Molten FeCr...CIN3	45–75	<0.10	<1.5	<0.03	2–4	<0.025
Sintered FeCr...CIN7					2–4	
					4–10	

*Chromium content is chosen from 50%, 60%, or 70% Cr with $\pm 5\%$ tolerances (i.e., 45% to 75% wt. Cr).

2. Silicon decreases nitrogen solubility; in the Fe-70%Cr melt, the addition of 1.5% Si drops solubility by 0.2% to 0.25% N.
3. Titanium and vanadium increase nitrogen solubility limits but do not substantially affect the kinetics of the process.
4. Oxygen significantly affects nitrogen solubility; furthermore, it also decreases the solubility rate. Therefore, FeCr melt must be deoxidized before the nitriding procedure (also, nitrogen gas must be dry, with the least amount of water possible).

The melt composition also has an impact on nitrogen concentration. Figure 8.20 represents phase equilibria of nitrogen with the Fe-Cr system at 1600°C. As the figure shows, 2% to 4% wt. N fits solubility limits for alloys near the Fe-70%Cr compositions. For >80% Cr it is not possible to have a homogeneous liquid phase, as hexagonal packed (HCP) $(\text{Cr}, \text{Fe})_2\text{N}$ or BCC solid solution forms at this temperature. The liquidus–gas line defines practically achievable nitrogen concentrations.

Therefore, it is possible to reach higher nitrogen contents only in the solid state. However, despite a lower nitrogen content in the molten FeCrN, the resulting alloy has high uniformity of composition and high efficacy of nitrogen utilization when added into a steelmaking furnace or ladle.

“Sintered” FeCrN is produced from solid powder of either low- or high-carbon ferrochrome. In the latter case, high-carbon FeCr must be first

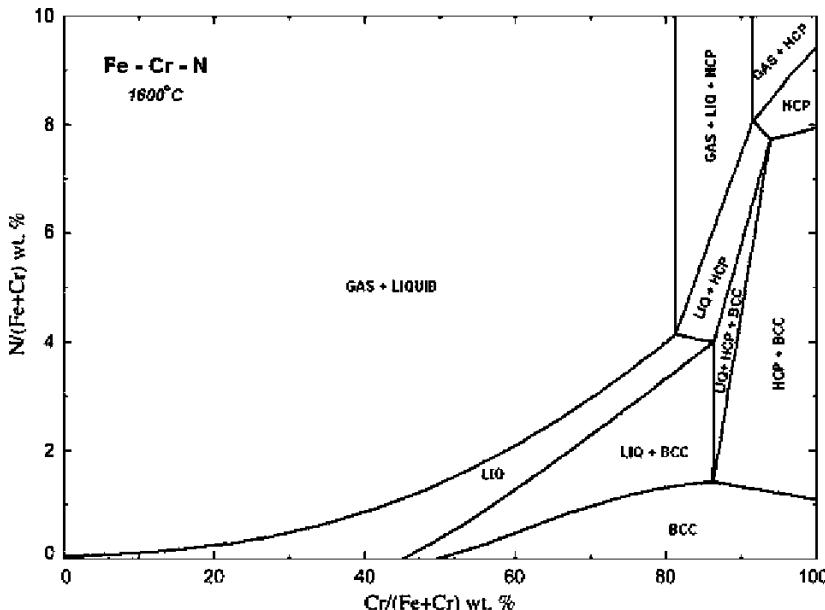


FIGURE 8.20 Phase equilibria in the Fe-Cr-N system at 1600°C.

decarburized in a vacuum to remove excess carbon. In this process as a rule, initial amounts of phosphorus and sulfur are retained in the alloy, so the quality of FeCrN by these impurities is determined by the quality of the initial ferrochromium. Although about 10% wt. N might be achieved in solid-state nitriding, the use of this alloy is not always reasonable due to increased nitrogen losses in steelmaking (particularly in a ladle) if the nitrogen content in the FeCrN is too high (lower efficacy).

Solid nitriding of high-carbon FeCr is carried out using lumpy FeCr briquettes at temperatures of 950° to 1050°C and 1 atm of nitrogen gas. This nitriding stage follows immediately after the vacuum treatment to remove carbon. Nitrided alloy cools down at low nitrogen pressure until 600° to 650°C; after that the cooling proceeds in air. Nitrogen in such FeCrN is present in the form of HCP $(\text{Cr}, \text{Fe})_2\text{N}$ and FCC $(\text{Cr}, \text{Fe})\text{N}$ phases.

Solid nitriding of low-carbon FeCr does not involve stages of decarburization, but the initial alloy has to be ground in smaller particles and then briquetted. This method is more economical as it does not require vacuum treatment and the homogeneity of FeCrN is higher than in the case of high-carbon FeCr. It is possible to use different starting alloys and obtain nitrided master alloys with Cr, Mn, and V.

Finally, it is also possible to get nitrided alloy simultaneously with smelting during reduction by aluminum in the presence of nitrogen, but this method usually does not allow more than 2% wt. N.

8.4 PRODUCTION OF METALLIC CHROMIUM AND ITS ALLOYS BY ALUMINUM REDUCTION

There are several methods of manufacturing pure chromium and its alloys by reduction of raw materials with aluminum. Practically, chromium chloride, iodide, and oxide might be used in alloys production. The main difference between chloride and iodide technology is that chlorides are being reduced (besides aluminum reduction; also use of sodium, magnesium, and zinc for chrome reduction has been developed), whereas iodides are thermally dissociated to pure chromium and iodine. The reduction of chromium oxide is commonly done using aluminum.

Metallic chromium is used to produce nickel- and cobalt-based superalloys and alloys with regulated low iron or without iron. There are also special chromium-rich alloys where iron content is limited. The properties of these alloys are very sensitive to impurities and therefore chromium, much like other pure components, has an extensive list of allowable limits (Table 8.15). This also puts additional demands on charge materials used for chromium processing (chrome oxide, aluminum powder, lime, etc.).

Basically all CrCl_3 reduction reactions are exothermic, so the process temperature rises by 200° to 250°C. This is beneficial, as the product mix is further subjected to vacuum distillation to remove resulting chlorides (AlCl_3 ,

TABLE 8.15 Nominal Composition of Metallic Chromium, wt. %*

Cr (min)	99A	99	98.5	98	97
Si	0.3		0.4	0.5	
Al	0.2	0.5		0.7	1.5
Fe	0.6			0.8	1.2
C	0.03			0.04	0.05
S	0.02			0.04	
P	0.02			0.03	
Cu	0.01		0.02	0.04	0.05
As	0.01				
Bi	0.0005				
Sb	0.008				
Zn	0.006		0.01		
Pb	0.0008		0.01		
Sn	0.004				
Co	0.005				
N	0.04	0.05			

*Empty cells means this impurity is not specifically controlled. Nitrogen content could be decreased to <0.015% wt. N on demand.

ZnCl_2 , MgCl_2 , or NaCl) over 950°C . Metallic chromium produced by this method normally has purity of 99.3% to 99.7% Cr.

The production of metallic chromium by the iodide method relies on a similar technique developed for pure titanium, hafnium, and other elements that form iodides capable of being properly refined and decomposed at heating. The interest in pure chromium made by this method is in low ductile-to-brittle transition temperature, which might reach $-50\ldots -65^\circ\text{C}$ for doped chromium or even -130°C if CrI_3 has been refined to achieve “extreme” purity of chromium, about 99.995% Cr. This method is rather expensive and is used only when special quality materials are demanded.

The most common metallurgical method is reduction of chromium oxide (98% to 99% Cr_2O_3) by other metals, especially aluminum. The classical method includes ignition or heating of the charge with chromium oxide, aluminum powder and sodium nitrate as an oxidizer. The mixture might be

composed as either exothermic (excess Al and NaNO₃) or endothermic (will require extra heating to keep the process). Use of nitrate, however, does not allow receiving chromium with less nitrogen. This might be improved by using magnesium as a reductant: heating up the mixture of magnesium and chromium oxide in an argon atmosphere leads to the evaporation of magnesium and the reduction of chromium powder with MgO as a side product. Another method is to replace sodium nitrate with calcium chromate CaCrO₄. The charge consisting of 37 kg of calcium chromate and 46 kg aluminum powder per 100 kg of chromium oxide was shown to achieve 0.03% to 0.05% N in the final ingot. This also could be carried out in an electric furnace, when at least part of the chromium oxide is melted first, forming slag with <50% CaO. Yet another method involves the reduction of chromium oxide with iron-less Cr-Si alloy, but the benefits of this method are questionable because iron-free chromium-silicon alloy requires a special preparation of its own. Thus, reduction of chromium oxide by aluminum is the most widespread process at the moment.

Theoretically, the reaction of chromium oxide with aluminum leads to the formation of metallic chromium and aluminum oxide. The latter starts to form solutions with the remaining chromium oxide, decreasing its activity and making further reduction more difficult. This is managed by adding flux (lime), which forms stable calcium aluminates and releases chromium oxide, improving reduction efficiency. Additionally, CaO decreases the liquidus temperature of the slag and (in oxidizing conditions) forms calcium chromite-chromate 9CaO4CrO₃Cr₂O₃, which is beneficial when making chromite-lime melts first. When the ratio CaO:Al₂O₃ = 0.5 to 1 in the ternary system CaO-Al₂O₃-Cr₂O₃, the saturation concentration of chromium oxide is normally below 8% wt., depending on temperature. Process slag additionally contains some MgO, SiO₂, and alkalis. The major factors affecting residual Cr₂O₃ content in the process slag are the ratio CaO:Al₂O₃ and the content of aluminum (its activity) in liquid chromium melt. For ~0.5% Al in the reduced chromium metal, the calculated equilibrium concentration of Cr₂O₃ in the slag varies from 0.001 to 0.5% wt.

Besides chromium oxide, formation of “CrO” should be taken into account, especially when the temperature is high and slag basicity is low. In this case, the calculated equilibrium concentration of “CrO” in the slag is about 1% to 2% wt. Experimental measurements, however, indicate that residual chromium content in slag is higher than expected by thermodynamic analysis, which might be limited for kinetic reasons. Some errors in residual chromium content in the slag might be due to the difficulty of metal droplets separation as slag is viscous and possibly heterogeneous (when Cr₂O₃ content is still high).

There are two technological methods of chromium oxide reduction by aluminum: off-furnace smelting and in an electric furnace. The principles of the processes are the same, but the charge composition and smelting procedures are different.

For the off-furnace method, about one tenth of the charge amount is loaded in a melting hearth and topped by the ignition mixture (magnesium and sodium nitrate). Upon ignition and formation of the melt, the rest of the charge is gradually loaded, trying to keep the charge melting rate in the range of 120 ± 10 kg/m²·min. For 1 t Cr, the materials consumption is 1650 kg of oxide, 630 kg of aluminum, and about 140 kg of sodium nitrate (lime content varies depending on the process). After the smelting has finished, the hearth is cooled down for about 10 h and the metal block is separated from the slag and crushed. Such chromium metal normally consists of 98% to 99.5% Cr, up to 1% Al, <0.3% Si, <0.6% Fe, <0.02% C, P, and S respectively, and <0.1% to 2% N. The extraction of chromium from oxide is about 90%.

In the case of special requirements for chromium purity, smelting and casting are carried out in under-pressure chambers (Fig. 8.21). There the charge consists of chromium oxide (>99% Cr₂O₃), aluminum powder, calcium chromate, and CrO₃ as an oxidizer (sodium nitrate is not used in this case). The charge is not loaded directly, but pelletized first at 400° to 500°C with the removal of water and possible carbon. The metal chromium that results from this method has 0.001% to 0.01% N, 0.001% to 0.01% C, <0.08% Fe, <0.03% Si and other nonferrous metals.

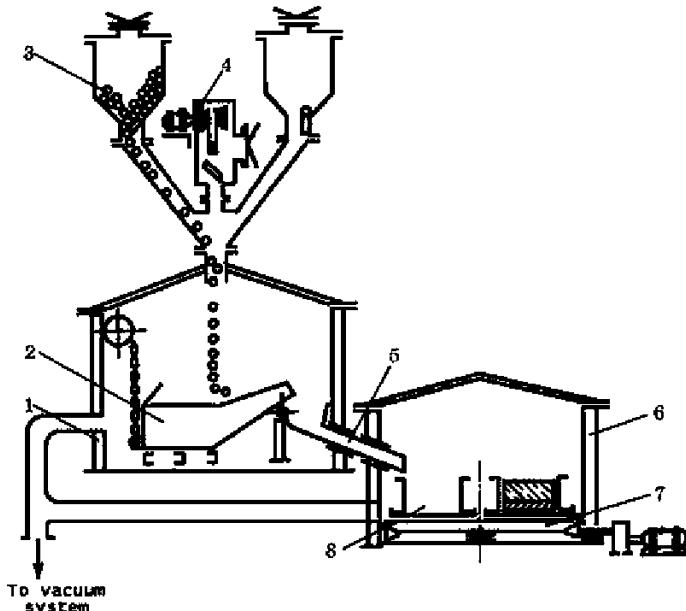


FIGURE 8.21 Two-chamber system for smelting pure chromium under a vacuum or inert atmosphere. 1, melting chamber; 2, tilting smelting ladle; 3, pellets storage; 4, ignition of the charge; 5, tapping channel; 6, casting chamber; 7, rotating table; 8, casting molds.

TABLE 8.16 Charge Composition for Low-Carbon FeCr Smelting Using Aluminum Reduction

Smelting Method	Off-Furnace	Furnace + Block	Furnace + Tapping of the Alloy
Charge materials, kg/t			
FeCr:			
Chromite	2215	1756	1640
Aluminum	710	466	445
Sodium nitrate	411	32	30
Lime		466	335

This technology for smelting of chromium has disadvantages such as low utilization of the smelter, high share of labor, and large consumption of refractories. Another version of this method is adapted to produce high-alumina slag in combined process. The smelting hearth (a tilting reactor) is lined by MgO bricks and has a seed of chromium metal up to 250 mm thick. The ignition proceeds in a method similar to the one described previously, but the melt is poured into an iron mold. Slag corresponding to approximate composition $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ forms an auto-crucible skull (“frozen lining”). The liquid slag is poured into an electric furnace, where lime and aluminum are added to ensure final chromium extraction.

The method could be also carried out essentially in an electric furnace, without the use of molds. As in the off-furnace method, one tenth of the charge is loaded into the furnace (without the ignition mixture) and the exothermic reactions are initiated by electric arc heating. Then about one fifth of the charge is added and the oxide–lime melt is formed in parallel with the reduction products (chromium melt). After formation of the melt, the rest of the charge is added. Upon completion, the cooling and separation of the chromium metal block is similar to that in the off-furnace process.

A tilting reactor is also used in the process of low-carbon (<0.04% C) ferrochromium (70% to 75% Cr) smelting using aluminum reduction. The main difference with the chromium smelting process described earlier is that chromite concentrate is used instead of pure chromium oxide (Table 8.16). Chromite concentrate for this process has 57% to 60% Cr_2O_3 , <2% SiO_2 , and about 10% Al_2O_3 and 14% MgO. The exothermic heat released during reaction is enough to reach melt temperatures above 2300°C. Chromium extraction using this process is about 90%. When lower-grade raw materials are used, it is still

TABLE 8.17 Typical Slag Compositions for Chromium Processing by Aluminum Reduction

Smelting Process	Cr (no lime added)	Cr (added lime)	Low-Carbon FeCr
Composition, wt. %	45% to 55% $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, 33% to 45% corundum ($\alpha\text{-Al}_2\text{O}_3$), <1% chromium spinel	75% to 80% Al_2O_3 , 6% to 12% CaO , 6% to 8% Cr_2O_3 <1.5 Na_2O	60% Al_2O_3 , 2% to 4% Cr_2O_3 , 10% to 13% CaO , 20% to 24% MgO , <1% FeO <1.5% SiO_2
Typical slag utilization routes	As raw material for making synthetic slag for ladle steel treatment		As raw material for production of high-alumina refractory cements (70% to 65% Al_2O_3 , 17% CaO)

possible to get standard low-carbon FeCr, but the utilization of chromium is also lower (70% to 80%) ([Eissa et al., 2010](#)).

The slag from aluminum reduction processes has different compositions, depending on the type of smelting method applied and the addition of lime ([Gasik et al., 2009](#)). These differences are summarized in [Table 8.17](#).

8.5 ENVIRONMENTAL ISSUES OF CHROMIUM AND ITS FERROALLOYS PROCESSING

As for all ferroalloys manufacturing processes, ferrochrome and other chromium alloys production is accompanied by the formation of different emissions (dust, fumes, organic compounds, wastewaters). Technological, medical, and sanitation studies have been devoted to the study of the sources of gas and dust formation, the composition of dusts and their effect on the environment, and the health of personnel ([Lyakishev and Gasik, 1998](#); [Stockmann-Juvala et al., 2010](#)).

8.5.1 Human Health Hazards of Chromium and Its Compounds

As a trace element, chromium is necessary in physiological doses to regulate metabolic processes in the body, and a person's daily chromium requirement is 0.2 to 0.25 mg. However, when it enters the body in larger doses, chromium may have a toxic effect on the organism ([Lyakishev and Gasik, 1998](#)).

In a lump state, metallic chromium and all groups of FeCr and FeSiCr are nontoxic in the conditions of their transportation, storage, and use. Dust of metallic chromium and of all chromium ferroalloys might, however, be

hazardous with respect to its degree of action on the human body. Midander et al. (2010) have studied the surface composition of ferrochromium particles ($<63\text{ }\mu\text{m}$) and confirmed that the surface is composed mainly of chromium and iron oxides, but there is also some enrichment of silicon (a few percentages when the bulk content of silicon is 1 wt%). It was shown that FeCr alloys cannot be assessed on their biological response based on pure components data and specific studies are required. Very low amounts of chromium and iron ($<0.15\%$) were released from particles of FeCr and FeSiCr alloys in synthetic biological media of varying pH and composition, and this chromium was released as Cr^{3+} . Disruptions of the external respiratory function (bronchial permeability) as well as nose and skin irritation have been observed historically when workers have been occasionally exposed to high Cr-rich dust levels (Lyakishev and Gasik, 1998). It is unlikely that Cr^{6+} compounds would form in technological smelting processes, unless there is some malfunction or excess oxidation of chromium-rich dust in off-gas tracts and wastewaters.

Inhalation exposure limit values for chromium oxide Cr_2O_3 and metallic chromium were set in the human health hazard assessment of trivalent chromium compounds conducted by the World Health Organization (WHO) (Stockmann-Juvala et al., 2010). The conclusions were based on the repeated dose inhalation study. The limit value for workers has been set at 0.5 mg Cr/m^3 air. Based on the metal release and surface composition of ferrochromium, the same value was suggested as relevant for ferrochromium as well (Stockmann-Juvala et al., 2010).

8.5.2 Dust and Wastewaters Treatment from Chromium Ferroalloys Processing

Many data have been collected for dust emissions of ferroalloys plants (Kasimov et al., 1988). Dust composition varies significantly, not only by process type but also by the gas cleaning method (dry/wet) and the dust sampling position (after furnace, after bag filters, venturries, cyclones, electrostatic precipitators, etc.). In respect to Cr_2O_3 content, dust usually has the highest values when the alloy produced has maximum chromium content and a minimal amount of carbon and silicon. For example, bag filter dust was reported to have 23% to 37% Cr_2O_3 for low-carbon Fe-Cr, decreasing to 13% to 22% for high-carbon FeCr and further $<1\%$ for FeSiCr (Lyakishev and Gasik, 1998). Chromium normally is reported as Cr_2O_3 , although some part might be oxidized to a hexavalent state ($<1\%$ CrO_3). Similarly, silica content is the highest for silicon-rich alloys processes (for FeSiCr up to 85% to 90% SiO_2) and silicon-reduction methods. Other major dust compounds are usually CaO , MgO , Al_2O_3 , and FeO . Naturally when dust has high chromia content, recycling of the dust into the FeCr production (via pelletizing) improves chromium utilization. In this method the dust captured is added to chromite ore concentrate, coke fines, and binder. Pellets are fed into the preheated furnace, and this

might completely utilize chromium-containing dust (Lyakishev and Gasik, 1998).

Whereas dust from the furnaces off-gas forms in preferably reducing conditions, dust from the roasting of pellets or chromite-lime mixture forms in oxidizing conditions. This is the major source of Cr⁶⁺ compounds to be monitored. For instance, calcium chromite–chromate $9\text{CaO}\cdot 4\text{CrO}_3\cdot \text{Cr}_2\text{O}_3$ and calcium chromate CaCrO₄ were detected in the most finely dispersed fractions of the dust of chromite–lime roasting furnaces. Hexavalent chromium is known to be toxic and carcinogenic (lung tumors are typical), unlike trivalent chromium.

Typical wastewaters from the production of various chromium compounds and the treatment of chromite ores contain hexavalent chromium Cr⁶⁺. Existing water quality regulations have strict limits on the permissible contents of chromium of different valences. Different methods have been suggested for the removal of chromium from waters, such as treatment with formic acid (precipitation of insoluble chromium formiate), ferrous sulfate $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (as the reducing agent for Cr⁶⁺), alkaline (NaOH) in the organic phase extraction (in the form of Na₂CrO₄), electro-coagulation, high-molecular ion exchange resin, activated carbon (absorption), bacterial method, and so on—even waste tin-plated metal cans (reduction of chromium followed by precipitation with limestone) (Lyakishev and Gasik, 1998).

8.5.3 Fire and Explosion Hazards of Chromium Ferroalloys

In a lump state, all chromium alloys are nonflammable and do not present fire or explosion hazards during their transportation, storage, and use. However, fine dust of the alloys may ignite depending on the degree of dispersion and the concentration of metallic particles. Experimentally it was established that for pure chromium dust aerosol, the flammability limit is 1000 mg/m³ air and ignition temperature 515°C and for FeSiCr (50%Si, 32%Cr) aerosols—1000 mg/m³ air and 625°C, respectively (Lyakishev and Gasik, 1998). On the contrary, no other ferrochrome alloy fines (<50 µm) explode or ignite in air <1000°C and <5000 mg/m³.

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