

# Complex Ferroalloys and Other Master Alloys

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## Chapter Outline

<b>20.1 Complex Ferroalloys</b>	<b>495</b>	20.1.3 Ferroalloys with Other Elements	498
20.1.1 Relevancy of Complex Ferroalloys Development	495	<b>20.2 Ferroalloys with Nonmetallic Elements</b>	<b>500</b>
20.1.2 Ferroalloys and Master Alloys with Aluminum	496	<b>20.3 Exothermic Ferroalloys</b>	<b>503</b>
		<b>References</b>	<b>504</b>

## 20.1 COMPLEX FERROALLOYS

### 20.1.1 Relevancy of Complex Ferroalloys Development

Complex ferroalloys and master alloys are used in steel and special alloys manufacturing for alloying (and composition adjustment) and refining (oxygen, sulfur, etc. removal) purposes. Historically, complex ferroalloys have been made by fusing (smelting) several ferroalloys and then tapping and casting, and classifying them into relevant sizes. However, this method is not very economic—once produced, ferroalloys must be again heated, melted, and processed. This leads to substantial energy and material losses and possibly more environmental pollution. Therefore, it has been suggested that complex alloys might be co-reduced and co-smelted directly from raw materials, similarly to the process used to separate ferroalloys (Gasik et al., 2009). A good example of this processing is the smelting of silicomanganese (SiMn), discussed in Chapter 7, where both silicon and manganese are co-reduced into a joint alloy.

The complex alloys presented in this chapter are essentially alloys (1) with more than two alloying elements, (2) produced from raw materials (i.e., usually not just by co-melting already made ferroalloys), and (3) aimed at the synergetic utilization of materials and energy. The last factor means that the co-reduction of several elements usually is based on a substantial decrease of their activity (better extraction of elements) and melting temperature (formation of eutectics, etc.), which is particularly important in the case of rare and expensive metals, as well as refractory metals (W, Mo, Nb, Ta). For example, the melting temperature of ferrotungsten (FeW) might be too high for its fast dissolution in liquid steel. With the creation of complex ferroalloys, this feature might be substantially improved. Another example of advantages of complex alloys is more controlled nonmetallic inclusions formation in steels. The use of silicon, manganese, and aluminum together allows more efficient deoxidation and delivery of the elements in situ, which is impossible if FeSi, FeMn, and Al are added separately (Vikhlevshchuk et al., 1987).

As requirements from the steelmakers differ depending on the steel grades produced, this stipulates a variety of different complex ferroalloys. This chapter lists the most common compositions and their applications, although some producers might have their own recipes. Some integrated steel plants may also employ in-house production of specific complex ferroalloys.

### 20.1.2 Ferroalloys and Master Alloys with Aluminum

Typical compositions of complex ferroalloys with aluminum are shown in Table 20.1 (Gasik et al., 1975, 1988).

Ferroaluminum is produced in large, closed, submerged arc furnaces. The raw materials normally include electrocorundum (fused  $\text{Al}_2\text{O}_3$  from refining smelting of bauxites or similar materials), steel chips, and coke. The process is flux-less with a low slag formation (<3% of metal mass). Smelting is continuous, and metal and slag are tapped periodically (~2 h). Slag contains 4% to 8%  $\text{SiO}_2$ , 2% to 3%  $\text{FeO}$ , 10% to 15%  $\text{CaO}$ , <1%  $\text{MgO}$ , and a balance that consists of  $\text{Al}_2\text{O}_3$ , and it usually has no tapping problems. However, for higher-grade FeAl (>30%Al), there is a possibility of aluminum carbide formation, so care must be taken to ensure carbides are eliminated during formation of the alloy (Gasik et al., 1988).

It is also possible to produce nitrided ferroaluminum (FeAlN) containing 4% to 10% N by solid-state nitriding of the alloy lumps in nitrogen or ammonia at 1200° to 1250°C, using a process similar to the one used to produce nitrided manganese and ferrochromium.

Ferromanganese–aluminum (FMA) alloy is used especially for deoxidation and alloying of high-quality tube steel and improves its properties at low (subzero) temperatures. Earlier technology of FMA alloys required dissolving aluminum in liquid medium carbon ferromanganese (MC FeMn), but since then the technology of smelting with carbon reduction has been developed. One

feature of this process is the use of the charge as fused alumina material (electrocorundum), as in the FeAl production process. The presence of liquid FeMn supports easier reduction of aluminum from the oxide, which lowers the temperature of alloy formation. Joint deoxidation of steel with FMA has shown an increased utilization of manganese and aluminum in comparison with their separate additives. The charge for FeMnAl smelting is composed of fused alumina, HC FeMn, steel chips, and coke. Slag formation here is also minimal, 1% to 2% of the metal mass. Smelting is continuous and tapping usually occurs every 2 h, as in FeAl smelting (Gasik et al., 1988).

Ferrosilicon–aluminum, also known as feralsit, alsimin, or FSA, is a complex steel deoxidizer as well as reductant used to process other ferroalloys that utilize reduction by silicon and aluminum (FeMo, FeV, etc.). The smelting process is carried continuously in submerged arc furnaces of 16 to 33 MVA power capacity. Charge materials include fused alumina, as in FeAl and FeMnAl processing, but here lower-grade aluminum and silicon sources also can be used, such as coal beneficiation wastes (ash, coal-dressing residuals, etc.) if their Al/Si ratio is suitable. This ratio should be selected according to the requirements in final steel composition, but also taking into account the stability of the FSA alloy during storage (Gasik et al., 1975). Thus, most FSA composition has Al:Si = 1:(4 to 6), although higher is also possible for a higher aluminum percentage (see Table 20.1). Additional charge materials are iron (steel) chips, FeSi, and coke. The ratio and the presence of FeSi are dictated by the composition of mineral charge components (FeSi is added if the SiO<sub>2</sub> concentration there is too low).

The technology of FMA and FSA alloys is also suitable for the production of ferrosiliconmanganese–aluminum alloys (FAMS). This alloy is a well-known efficient deoxidizer in comparison to separate additions of aluminum, ferrosilicon, and ferromanganese. The reduction of ferroalloy consumption in this case might be 15% to 30%, increasing the share of deoxidation in the ladle by 30% to 70%. Alumina–silica raw materials (basically, any suitable mineral combination might be used) are briquetted with carbon reductant and smelted with silicomanganese (20% Si), coke, and possibly extra steel chips. Although manganese ore or high-MnO slag could be used as a manganese source, in practice it is not recommended due to a much lower melting temperature of the charge and premature slag formation. Using stavrolite mineral concentrates (46% to 50% Al<sub>2</sub>O<sub>3</sub>, 36% to 38% SiO<sub>2</sub>, 13% to 15% Fe<sub>2</sub>O<sub>3</sub>) the resulting FAMS alloy contains 10% to 14% Al, 22% to 24% Mn, 10% to 15% Si, about 0.3% to 0.5% Zr, and 1% to 2% C. A low phosphorus content is essential (see Table 20.1) to prevent this alloy from decomposition upon storage. It was found that phosphides (AlP) in the alloy react with moisture to form poisonous phosphine (PH<sub>3</sub>), which transforms alloy into a dust form (Gasik et al., 1988).

The addition of components with higher CaO content allows the reduction of some calcium and the formation of the more complex Fe–Al–Mn–Si–Ca alloy (see Table 20.1). This alloy has a special application in nonmetallic inclusion control

in steels: calcium promotes dispersed and globular forms of the inclusions, which is important, for example, in ball-bearings steels (Gasik et al., 1975).

Chromium and ferrochromium have a relatively low deoxidizing ability compared to aluminum and silicon, so the Fe-Cr-Al complex ferroalloy is a good option for the combination of deoxidizing and alloying properties. Upon addition to the liquid steel, these alloys quickly dissolve, which reduces the duration of their contact with the air (lower oxidation and nitridation). FeCrAl alloys are produced by reducing chromium oxide raw materials with aluminum in the presence of a large excess of aluminum in the charge mixture.

Some plants produce ferrochrome–aluminum prepared by dissolving aluminum in liquid ferrochrome, but as mentioned this route is not very economic. Additionally, production of FeCrAl by the aluminothermic method allows lower phosphorus content in the alloy in comparison with the method whereby FeCr and Al are fused. Ferro-chrome-aluminum is produced in a single step in ferroalloy furnaces by carbon reduction of fused alumina (or a similar alumina source, such as kyanite) in the presence of charge ferrochrome or ferrosilicochrome (Gasik et al., 1988).

Among other master alloys with aluminum, which are produced mainly by aluminum reduction, those with molybdenum, tungsten, and chromium might be mentioned (see Table 20.2). These master alloys have a limited amount of iron in comparison with those shown in Table 20.1, as their main application is the production of nonferrous alloys (nickel superalloys, aluminum alloys, etc.).

### 20.1.3 Ferroalloys with Other Elements

The common complex ferroalloys, which are not based on the reduction of aluminum, are usually of the Fe-Cr-Mn-Si system. These alloys (Table 20.3) are used, for example, to manufacture special Cr-Mn stainless steels where low carbon (LC) FeCr or FeSiCr and manganese metal have been traditionally used, but separately (Gasik et al., 2009).

Complex ferrochrome–manganese alloys (FeCrMn) are a useful option to reduce manganese evaporative losses and to decrease the FeCr melting temperature. Standard LC FeCr (~70% Cr) has a melting temperature of 1640° to 1680°C, but the addition of 30% to 35% Mn decreases it to 1400° to 1500°C, which is a positive factor for faster dissolution of the alloy in liquid steel. The advantage of FeCrMn alloy smelting is that lower-grade ores ( $\text{Cr/Fe} < 3$ ) might be used together with MnO-rich slag, using crude SiMn or FeSiCr as reductants. Chromium dissolves up to 70% Mn in the solid state, which assists in the decrease of manganese activity and improves the reduction process (Gasik et al., 1988).

This alloy with additional silicon (FeMnCrSi) could be produced by various methods. Besides the evident process of smelting different ferroalloys (fusion), reduction of MnO-rich slag and lime–chromite melt by FeSiCr or joint co-reduction of Mn, Cr, and Si sources by carbon might be applied. One method is to reduce dumped slag of manganese metal production (10% to 14% MnO;

**TABLE 20.1** Ferroalloys with Aluminum, wt. %, Balance: Iron\*

Alloy	Al	Mn	Si	Ca	Cr	C	S	P
FeAl10	8–12		<4			<3	<0.03	<0.04
FeAl15	12–17		<3.5			<3	<0.03	<0.04
FeAl20	17–22		<3.5			<2	<0.03	<0.04
FeAl25	22–30		<2			<1	<0.03	<0.04
FeAl35	33–37	<0.7	<0.5			<0.02		
FeAl40	~40	<0.7	<0.5			<0.02		
FeAl50	~50	<0.7	<0.5			<0.02		
FeMn45Al	12–16	40–50	<2.5			<1.5	<0.03	<0.3
FeMn55Al	12–16	50–60	<2.5			<1.5	<0.03	<0.3
FeMn65Al	12–16	60–80	<2.5			<1.5	<0.03	<0.3
FeSiAl <sup>†</sup>	18–22		40–45					<0.07
FeSiAl <sup>‡</sup>	48–50		35–37					
FeMnAlSi <sup>§</sup>	10–14	22–24	10–15			1–2		<0.06
FeMnAlSiCa	4–10	17–22	45–50	7–12				
FeCrAl	18–22		0.5–1		48–52			

\*Empty cells mean no data specified.

<sup>†</sup>Feralsit alloy.<sup>‡</sup>Alsimin alloy.<sup>§</sup>FAMS alloy

which already has a low phosphorus content) by FeSiCr. If the FeMnCrSi alloy smelting is organized cooperatively with manganese production, the liquid slag latent heat might be additionally utilized. Industrial practice shows a possibility of such FeCrMnSi alloy production with 0.01% to 0.013% P. Such an alloy is stable during storage.

A special category of complex ferroalloys is made up of niobium master alloys (Table 20.4). Although ferroniobium (FeNb) is suitable for many applications, in many cases its dissolution rate and melting temperature are too high for economic steelmaking (Patel and Khul'ka, 2001). This also concerns master alloys for non-ferrous applications (superalloys). The melting point of these alloys is less than 1400°C, and the rate of dissolution is two times higher than for the standard FeNb.

**TABLE 20.2** Composition of Aluminum Master Alloys, wt. % (Gasik et al., 1988; Gasik and Mazur, 2003)

Master Alloy	Al	Mo	W	Cr	Fe	Si	Ti
Al-Cr	15–40			60–85	<1	<0.5	
Al-Cr-Mo	30–40	30–36	1–8	23–27	4–7	2–5.5	
Al-Cr-Mo-W	28–33	24–28	12–19	18–21	5–8	<3	
Al-Cr-Ti	9–12	18–23		64–70	<1.8	<0.6	4–7
Al-Mo-Ti	38–48	48–52	1.5–5.5		<1.5		6.5–8
Al-Mo-W-Ti	46–52	26–32	11–15		<1	<2.5	7–9
Al-W-Mo-Ti	40–42	15–18	30–36		<0.8	<3.5	6–7
Al-W-Ti	48–58	5–6	40–43		<1	<2.5	4–6
Al-W-Cr-Mo	<2	2.5–4	30–40	50–60	<2	<0.8	

**TABLE 20.3** Composition of the Complex Fe-Cr-Mn-Si Alloys, wt. %

Ferroalloy	Mn	Si	Cr	C	P	S
FeMnSiCr	15–20	35–40	20–30	<0.03	<0.02	<0.05
	20–30	30–35	20–25	<0.04	<0.02	<0.05
	30–35	20–30	20–25	<0.05	<0.02	<0.05
FeMnCr	16–25	<1	45–54	<0.05		
	26–35	<1.5	39–49	<0.05		
	36–44	<1.6	31–39	<0.05		
	~45	<2	~30	<0.05		

## 20.2 FERROALLOYS WITH NONMETALLIC ELEMENTS

There are few ferroalloys with nonmetallic elements especially produced for steelmaking applications. Besides ferroalloys with boron (Chapter 17), those of industrial relevance are alloys with phosphorus, sulfur, and probably selenium, although some plants might have other forms of ferroalloys production.

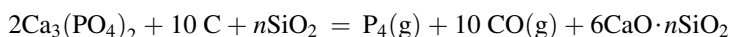
**TABLE 20.4** Some Niobium-Contained Complex Master Alloys

Ferroalloy	Nb	Mn	Al	Cr	Fe	Ni	Ti	Si	C
FeNb	20–30				Bal.				
FeNbMn	30–50	20–30			Bal.				
CrNb	60–88		<1	Bal.	<1		<1		<0.1
NiTiNb	7–12		4–8		<2	Bal.	15–23	<2	<0.1
FeNbTi	15–18		8–12		Bal.		27–38	<3	<0.2

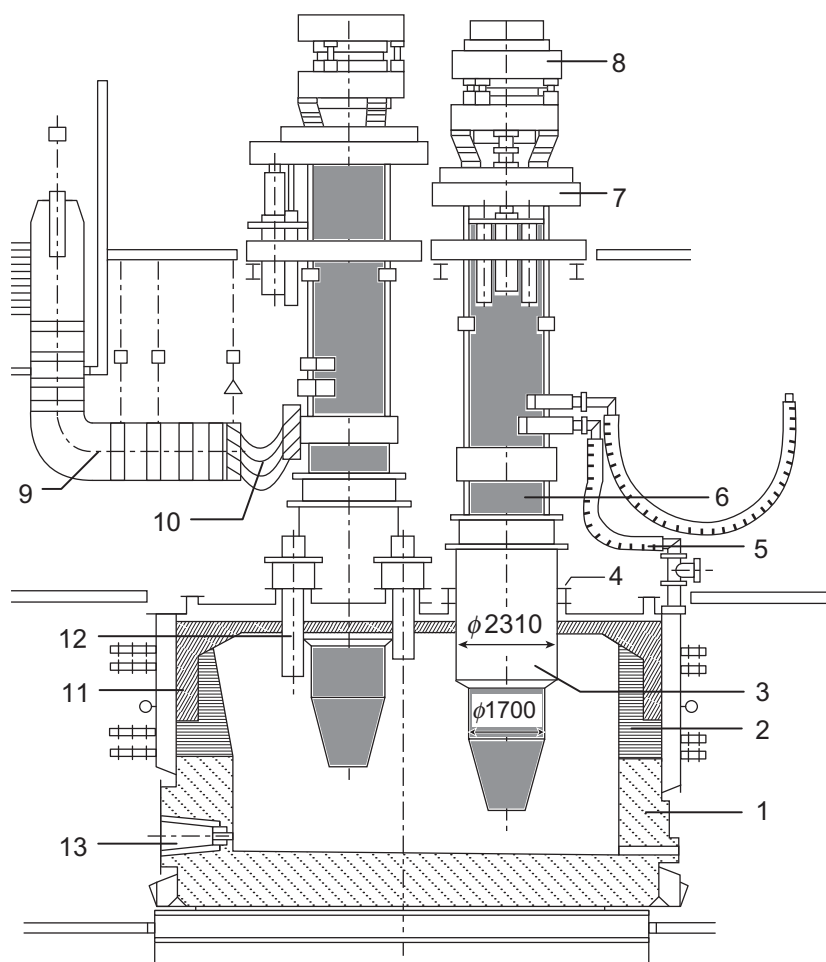
Ferrophosphorus might contain up to 24% to 28% P, and it is used in both lumpy and powder form. Powdered FeP is mainly intended for ferrous powder metallurgy applications as phosphorus is beneficial for liquid phase sintering and better “soft” magnetic properties (Antsiferov et al., 1999). In steels, phosphorus is usually an undesired impurity, but in some applications reasonable phosphorus content is beneficial. For example, phosphorus gray cast iron (0.5% to 0.8% P) is applied for the centrifugal casting of pipes and fittings, and some phosphorus in steel improves its machining feasibility. Cast iron with an even higher phosphorus content (2% to 5% P) is used for metallurgical equipment (cast iron molds for slag and metal, etc.). An increase of phosphorus up to 0.2% P in austenitic stainless steel (20% Cr, 10% Ni, 2% Mo) allows formation of a more fine dispersion of precipitates during heat treatment, increasing hardness and creep resistance (Gasik et al., 1975).

Ferrophosphorus could be produced in electric furnaces and in blast furnaces, but most FeP is produced by using by-product alloy of phosphorus production by carbon reduction of calcium phosphates. The process is implemented in closed (hermetic) submerged arc furnaces, as all reduced phosphorus vapor must be properly collected (Scheepers et al., 2010). The furnace power is 10 to 80 MVA, but there is a tendency to build and exploit larger power furnaces (60 to 80 MVA) with self-baking electrodes of 1700 mm diameter (Fig. 20.1).

Phosphorus is reduced from calcium phosphate melt by carbon from coke in the presence of silica flux (quartzite):



At the same time, iron and manganese oxides from phosphate charge are also reduced and form molten metal, which is periodically tapped and delivered as ferrophosphorus. Its exact composition depends on the quality and composition of phosphorite ore, but usually the alloy contains 15% to 30% P, 2% to 12% Si, and 2% to 4% Mn, the balance being made up of iron and other impurities (Gasik et al., 1975). Gaseous phosphorus is trapped from the gases by cooling



**FIGURE 20.1** Submerged arc furnace of 72 MVA with hermetic cover for phosphorus reduction: 1, shell; 2, lining; 3, electrode cylinder; 4, gasket; 5, furnace water cooling system; 6, electrode holder; 7, hydraulic lift; 8, electrode shifting mechanism; 9, short net; 10, flexible current bus bars; 11, cover; 12, charge feeders; 13, tap hole.

below 50°C under water, leading to a condensation of white phosphorus. The amount of ferrophosphorus is about 1.8% to 2.2% of the charged phosphorite mass.

As with phosphorus, sulfur is often regarded as an impurity in steels. However, steels that undergo machining operations are required to have a certain amount of sulfur content for proper chip formation (chip breakup upon turning, drilling, etc.). Sulfur is often added to steels and alloys in the form of ferrosulfur (28% to 32% S), if the use of other sulfur-containing compounds is not feasible for any reason (Zhukov et al., 1998).



Other chalcogenides—especially in the form of ferroselenium with 25% to 50% Se and ferrotellurium (<50% Te)—are also used for the same purpose (Gol'dshtein et al., 1979). Selenium and tellurium improve the machinability of steels (up to 0.05% to 0.30%). Their addition requires more care, as proper ratios of  $Mn/(S + Se + Te)$  and  $S/(Se + Te)$  have to be maintained for optimal effect (Zaslavskii et al., 1969). When selenium is absent, sulfur in steel is usually combined into  $MnS$ , which forms elongated nonmetallic inclusions at hot rolling, causing less corrosion resistance toward  $H_2S$ . The addition of selenium ( $Se/S \sim 0.8$ ) decreases this phenomenon two- to three-fold, leading to smaller globular inclusions. In comparison with sulfur's effect on machining, even minor selenium addition leads to the formation of complex compounds  $(Mn, Me)(S, Se)$ , improving significantly the lifetime of cutting tools at very high machining rates (Alferov and Belov, 1975). It was reported that microalloying with selenium reduces the loss of metal (scrap and rejects) due to metallurgical defects and also the tendency to form quench cracks. In terms of improved machinability with high-speed machining utilizing hard-alloy cutters, the addition of selenium is much superior to microalloying with lead, especially in machining that uses high-speed steels (Gol'dshtein et al., 1979).

## 20.3 EXOTHERMIC FERROALLOYS

These types of special ferroalloys (or, more precisely, mixtures of ferroalloys with exothermic compounds) are not widespread but are used from time to time to process special steels and alloys, especially in-house. The quality of exothermic ferroalloys is measured by several indicators: minimal temperature of the beginning of the reaction, temperature of the reaction of ferroalloys with liquid metal, and the optimum reaction rate considering particular steel grades. However, the basis is that the alloying should be done under a spontaneous metallothermic process.

The main components of the exothermic charge are a mixture of ferroalloys, oxidant, and possibly reductant (aluminum powder) and fluxes (calcium fluoride). Previously sodium nitrate was used as an oxidant, but it is not recommended because there is a risk that it will lead to an increase of nitrogen content in steel. Thus, traditional oxidants used now are potassium chlorate, oxides of chromium, manganese, and the like, which exclude nitrogen (Gasik et al., 1975).

Some typical compositions of exothermic ferroalloys and their properties are shown in Table 20.5.

As follows from the data in Table 20.5, most of these exothermic ferroalloys have been designed for implementation of alloying by Cr, Mn, W, Ni, and Nb, but this list can be greatly expanded.

Optimal grain size for the metal part of the exothermic charge is 1.5 to 2 mm. The other components (oxides, flux) should have a grain size of 0.2 to 0.5 mm. The calorific value of briquettes is usually within 33 to 84 kJ/g·atom, and

**TABLE 20.5** Some Properties of Exothermic Ferroalloys

Compounds	% wt.	Grain Size, mm	Heat effect, kJ/mol	Density, g/cm <sup>3</sup>
LC-FeCr or HC-FeCr	81	1.6	33.5	4.2
NaNO <sub>3</sub>	8.2	0.5		
FeSiCr	10.8	0.2		
LC-FeCr	87.2	1.6	33.5	4.1
KClO <sub>3</sub>	6.3	0.5		
FeSiCr	6.5	0.2		
LC-FeCr	61.6	1.6	5.44	4
Mn ore (55% Mn)	24	0.4		
Al powder	7.2	—		
FeSiCr	5.1	0.2		
CaF <sub>2</sub>	2.1	0.2		
FeMn	70	2	33.5	4.2
FeSiMn	19	0.25		
NaNO <sub>3</sub>	8	0.5		
CaF <sub>2</sub>	3	0.2		
W concentrate	67.8	0.5	62.8–79.5	4
Scheelite (CaWO <sub>4</sub> ) concentrate	17	—		
Al powder	15.2	—		
W concentrate	84	0.5	54.4	4.1
FeSi65	16	0.2		
NiO	71.2	0.5	73.5	3.5
FeSiMn	18.4	0.2		
FeSi75	6.5	0.2		
Al powder	3.8	0.2		

the recommended density is 3.5 to 4.2 g/cm<sup>3</sup>. Briquettes can weigh up to 20 kg, although smaller briquettes weighing up to 2 kg are also used. The strength of the raw briquettes is about 6 MPa, and their dry-state strength is 25 to 50 MPa (after drying at 90° to 120°C to remove 40% to 50% moisture, and then at 300° to 350°C to a moisture content of <0.1%).

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