

# Technology of Ferronickel

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## Chapter Outline

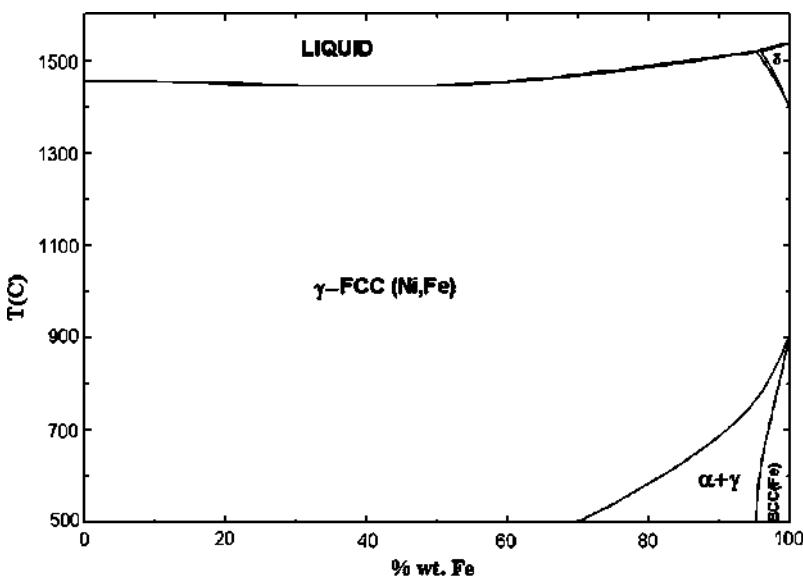
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## 10.1 PROPERTIES OF NICKEL AND ITS COMPOUNDS

Nickel (atomic number, 28; atomic weight, 58.6934) belongs to group VIII of the periodic table and together with iron and cobalt is commonly referred to as the “iron triad.” Indeed properties of these three elements are rather close. The outer electron shell configuration of the nickel atom is  $3d^84s^2$ , so its common valence is +2, and less often +3. Nickel’s melting temperature is 1455°C, and its boiling temperature is ~2915°C. The density of nickel is 8.92 g/cm<sup>3</sup> (i.e., slightly higher than that of iron).

Nickel is an important and widely used constituent of many alloy steels. It is a well-known solid solution strengthener and a promoter of high toughness, especially at low temperatures. Nickel has only one stable solid phase (FCC) in the whole practical temperature range, and its addition usually stabilizes the austenitic (FCC) structure in steels and alloys. This is an important application in stainless steelmaking (austenitic, martensitic, and duplex grade stainless steel compositions). Besides stainless, nickel is also widely used in low-alloys steels, and it is a major component of nonferrous, high-temperature-resistant superalloys and heat-, oxidation-, and corrosion-resistant materials.

With iron, nickel forms continuous solid solutions with austenitic (FCC) compositions (Fig. 10.1). In the liquid state, both elements have unlimited



**FIGURE 10.1** The equilibrium diagram of the Ni-Fe system. Magnetic transformations and possible intermetallics are now shown.

solubility. Earlier it was assumed that the Ni-Fe system's behavior is close to ideal solution, but then it was determined that the activity coefficient of nickel is lower than unity in alloys <40% Ni. There are also indications of the formation of an ordered  $\text{FeNi}_3$  structure below 500°C, although this process seems to be kinetically limited and possibly of a metastable nature.

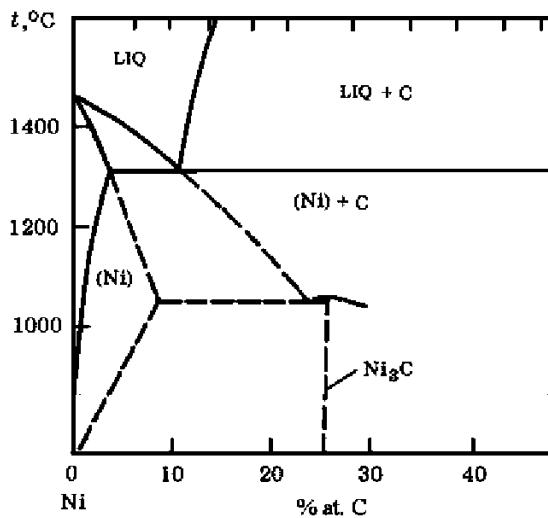
Like iron, nickel and carbon form carbide  $\text{Ni}_3\text{C}$  of a cementite type, but it is more metastable than  $\text{Fe}_3\text{C}$  and does not usually form easily. The stable phase diagram of the Ni-C system has a simple eutectic form with Ni-C eutectics at 1326°C (Fig. 10.2). Dashed lines in this diagram indicate approximate phase positions for metastable  $\text{Ni-Ni}_3\text{C}$  equilibria.

With silicon, nickel forms several stable silicides, some of which have a noticeable homogeneity range (Fig. 10.3). Silicon also dissolves in considerable amounts of liquid and solid nickel (Sudavtseva and Zinevich, 2004).

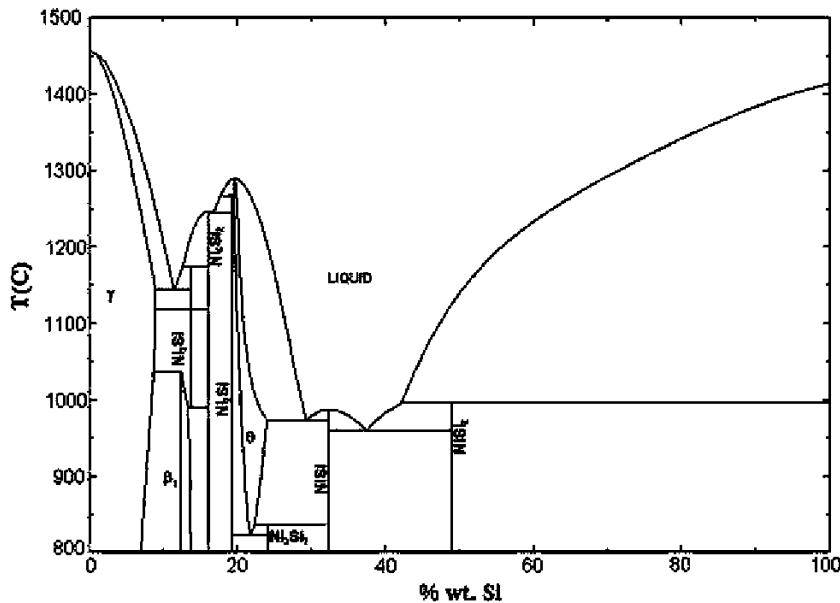
A number of intermetallic compounds are formed between nickel and aluminum (Fig. 10.4). The solubility of aluminum in the solid nickel is much higher than nickel solubility in solid aluminum.

With sulfur, nickel forms four sulfides:  $\text{Ni}_3\text{S}_2$ ,  $\text{NiS}$ ,  $\text{Ni}_3\text{S}_4$ , and  $\text{Ni}_2\text{S}$ . The most stable nickel phosphides are  $\text{Ni}_5\text{P}_2$ ,  $\text{NiP}$ ,  $\text{NiP}_2$ ,  $\text{Ni}_2\text{P}$ , and  $\text{Ni}_3\text{P}$  (Gasik et al., 2009). Phosphide  $\text{Ni}_3\text{P}$  is isomorphic to  $\text{Fe}_3\text{P}$  and  $\text{Mn}_3\text{P}$ .

Nickel dissolves a significant amount of oxygen (Fig. 10.5) and forms nickel oxides  $\text{NiO}$  and  $\text{Ni}_2\text{O}_3$ . The latter completely decomposes to  $\text{NiO}$  above

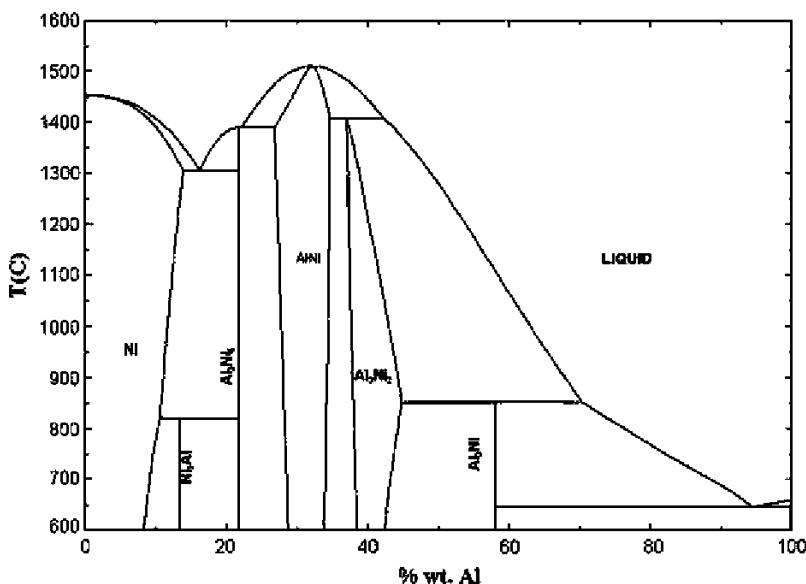


**FIGURE 10.2** Stable and metastable equilibria in the Ni-C system.

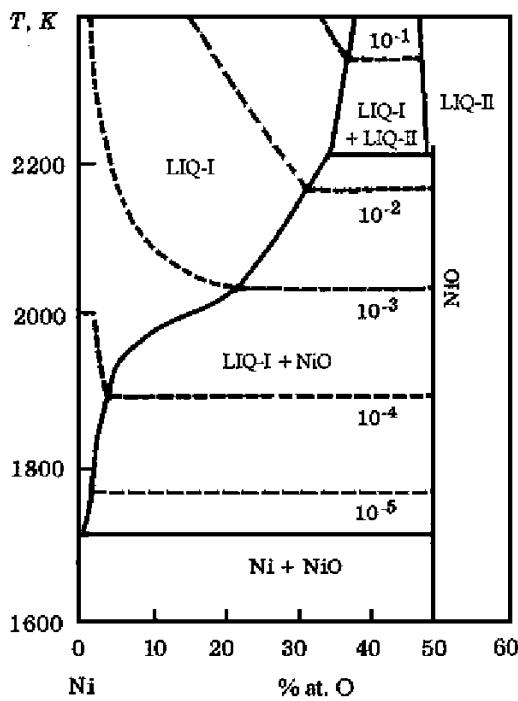


**FIGURE 10.3** The equilibria in the Ni-Si system.

1100°C and thus is not normally observed in the materials present during the smelting of ferronickel. Nickel oxide also forms binary compounds with silica ( $\text{Ni}_2\text{SiO}_4$ ) and ternary compounds with silica and calcia ( $\text{CaNiSi}_2\text{O}_6$ ).



**FIGURE 10.4** The equilibrium phase diagram of the Ni-Al system.



**FIGURE 10.5** The equilibrium diagram of the Ni-O system. Dashed lines represent equilibrium oxygen pressure, atm.

## 10.2 NICKEL RAW MATERIALS

Nickel appears in two different mineral categories, namely the sulfide type and the laterite type (oxide–silicate). Among known sulfide minerals of commercial interest are violarite  $\text{Ni}_2\text{FeS}_4$ , siegenite  $(\text{Co},\text{Ni})_3\text{S}_4$ , poldimitite  $\text{Ni}_3\text{S}_4$ , fletchrite  $\text{Cu}(\text{Ni},\text{Co})_2\text{S}_4$ , and others. These ores might contain up to 4% Ni, but their availability is about 14% of the total known nickel reserves. Thus, recovery of nickel from laterite ores is getting more attention, as laterite might have up to 1% to 2% Ni. Depending on the composition of the gangue, laterite ores are classified into magnesia-, silicate-, and alumina-type varieties. There are also known reserves of iron ore (50% to 60% Fe and 1% to 1.5% Ni), which might be classified into limonite and saprolite ores. Limonite ore has 1.2% to 1.3% Ni, <0.1% Co, <0.1% MgO, and 45% to 50% Fe. Saprolite ores have 2% to 2.3% Ni, 0.01% to 0.05% Co, 15% to 20% MgO, and 15% to 20% Fe. In ferronickel production, both lean ores (<1% Ni) and relatively nickel-rich ores (2% to 3% Ni) might be used. The lean laterite ore (Ukraine) has (wt. %) 0.9 to 1 Ni, ~20 Fe, 0.05 to 0.10 Co, 32 to 44  $\text{SiO}_2$ , 5 to 7  $\text{Al}_2\text{O}_3$ , 4 to 6 MgO, <2 CaO, and 1 to 2  $\text{Cr}_2\text{O}_3$ . The chemical composition of nickel ores varies widely from plant to plant—(% wt.): 1 to 3 Ni, 0.03 to 0.1 Co, 10 to 32 Fe, <28 MgO (Weisegar et al., 2005)—and thus different ores are blended.

Oxidized nickel ores are composed of many complex minerals, such as nontronite ( $\text{Fe}[(\text{OH})_2\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}]\text{Na} \cdot (\text{H}_2\text{O})_4$ ), as a group of smectites. Their general formula might be represented as  $\text{X}_{0.33}\text{Y}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , where X is Ca or Na, Y is  $\text{Fe}^{3+}$ , Al, Cr, Mg, Ni, Zn, Li. These mineral formations are usually composed of ~14%  $\text{Al}_2\text{O}_3$ , ~8% MgO, and small amounts of CaO, K<sub>2</sub>O, and Na<sub>2</sub>O, and in some cases also NiO and Cr<sub>2</sub>O<sub>3</sub>. Some of the clay-forming minerals are based on serpentine ( $\text{Mg},\text{Fe},\text{Ni}_{8-x}\text{Al}_x\text{Si}_{4-y}\text{Al}_y\text{O}_{10}(\text{OH})_8$ ).

Potential future sources of nickel, cobalt, and manganese minerals are manganese nodules in the ocean. It is estimated that stocks of nodule in the Pacific Ocean have more than  $10^{10}$  tons, containing up to 2.5% Ni, 0.1% to 2.6% Co, <1.9% Cu, and so on. However, all of these deposits are confined to the central regions of the deep ocean, so their exploration requires substantial investment and the development of new underwater mining technologies.

## 10.3 FERRONICKEL SMELTING AND REFINING

### 10.3.1 Ferronickel and Its Smelting

The standard ferronickel for steelmaking has a wide range of compositions, from 5% to 25% Ni, Table 10.1. Solar et al. (2008) noted two trends in nickel laterites processing, one favoring high-grade ferronickel (35% to 40% Ni) and the other favoring lower grades (20% to 25% Ni). Because the ores processed vary widely in terms of nickel content and other components, it is natural that both lower and higher reduction degrees are used. Low reductions imply higher

**TABLE 10.1** Typical Composition of Ferronickel Alloys

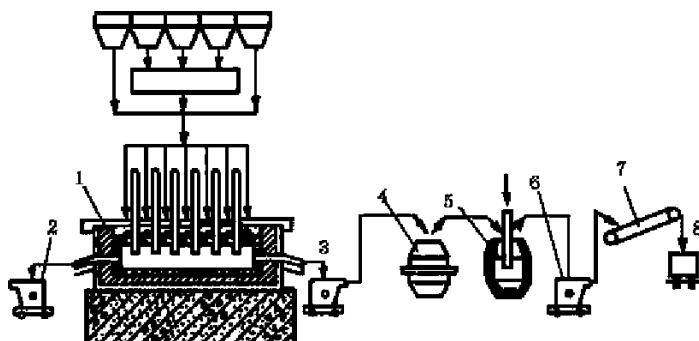
Grade	Ni	Co	Si	C	Cr	S	P
FeNi10	5–15	0.3–0.6	<0.3	<0.1	<0.3	<0.08	<0.03
FeNi15	12–18	0.5–0.8	<0.4	1–2.5	<2	<0.1	<0.03
FeNi20	15–25	*	<0.4	1–2.5	<2	<0.4	<0.03

\*Recommended value Ni/Co = 20–40.

slag losses and lower nickel recoveries but also lower power and reductant requirements, whereas higher reductions imply the reverse (Solar et al., 2008). In some cases, nickel scrap and remelts are added to low-grade FeNi to increase nickel content.

The technological scheme for ferronickel smelting in electric includes the following steps (Fig. 10.6): preparation and averaging of nickel ore; preparation, dispensing charge materials, and calcining the charge (ore, limestone, coal, and recirculated dust) in the rotating drum furnaces; FeNi smelting with a hot charge supply from rotary kilns, FeNi refining (sulfur removal) in the ladle, followed by purging with oxygen (first in a converter with an acid lining, then with the basic lining); and finally casting of refined ferronickel.

An example of the modern large-scale FeNi smelter was given by Rodd et al. (2010). The sources of sulfur in the charge are carbon reductant and heavy fuel oil (1.8% S) and phosphorus, mainly carbon reductant and nickel ore. The smelting of ferronickel using lean nickel ores usually starts with roasting (calcining) of the ore mixture with limestone (~one third of the ore), anthracite



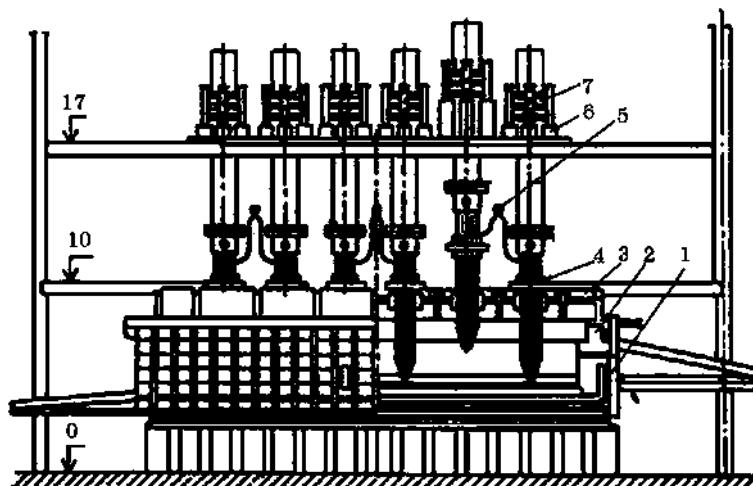
**FIGURE 10.6** Flow sheet of ferronickel production: 1, submerged electric arc furnace; 2, slag ladle; 3, ladle for crude FeNi; 4, converter with acid lining (removal of excess Si and Cr); 5, converter with basic (MgO) lining for phosphorus removal; 6, ladle for refined ferronickel; 7, filling/casting machine; 8, storage.

(~1/10 of the ore amount), and recycled dust. Roasting is carried out in rotary kilns (~3 m in diameter, ~75 m in length, with a hot zone length of 9 to 12 m in the case of lean ore processing). The treatment temperature should not exceed 850°C to avoid stacking of the charge in the kiln. The hot roasted charge is fed into the submerged arc furnace of 50 MVA with six 1200 mm electrodes (Fig. 10.7) operating at a 30 to 40 kA current.

This furnace hearth has dimensions  $\sim 25 \times 10 \times 5$  m, and it is lined with carbon blocks (see Fig. 10.7). The furnace has three tap holes for slag and three tap holes for FeNi. Other furnace types (e.g., the round type of 24 to 94 MVA) and novel developed DC furnaces (Jones et al., 1996) are also used for FeNi smelting (Walker et al., 2010). From 1 ton of roasted charge the yield of crude ferronickel is 120 to 140 kg and for slag it is 650 to 700 kg. The slag has <0.02% to 0.06% Ni, <0.02% Co and low basicity (50% to 52% SiO<sub>2</sub> versus 25% to 30% [CaO + MgO]), and its main utilization is as a construction material. Slag behavior and reactions during laterite smelting have been analyzed (e.g., by Utigard, 1994).

### 10.3.2 Refining and Casting of Ferronickel

Because crude ferronickel has a high sulfur content, it undergoes desulfurization in the ladle by sodium carbonate (soda):  $[S]_{\text{FeNi}} + 2 \text{Na}_2\text{CO}_3 + [\text{C}] + [\text{Si}] = (\text{Na}_2\text{S}) + (\text{Na}_2\text{SiO}_3) + 3 \text{CO}$ . The consumption of soda is ~4% to 5% by weight of FeNi metal, and a practically achievable degree of desulfurization is 50% to 60%.



**FIGURE 10.7** Ferronickel smelting furnace: 1, shell; 2, lining; 3, cover; 4, gaskets; 5, current bus bars; 6, electrode moving mechanism; 7, electrode shifting mechanism. Numbers indicate the height levels in meters.

Treated ferronickel is poured into the converter with acid lining and subjected to oxygen purge to remove excess chromium and silicon. An increase of silica in the slag facilitates the transition of chromium into the slag from ferronickel. This dump slag from refining ferronickel in an acid converter has the following composition (% wt.): 52 to 55 SiO<sub>2</sub>, 15 to 25 Fe, ~1.7 CaO, 2 to 6 MgO, 1 to 8 Cr<sub>2</sub>O<sub>3</sub>, ~3 Al<sub>2</sub>O<sub>3</sub>, and <0.09 Ni. After this refining stage, ferronickel is poured into the next converter with a basic lining and subjected to conversion with oxygen purge to remove phosphorus. The oxidation of phosphorus in the main converter in the presence of highly basic slag is similar for phosphorus removal in conventional steelmaking. The converted basic slag has the following composition (%): 15 to 20 CaO, 5 to 10 SiO<sub>2</sub>, 35 to 50 FeO, <0.05 Ni, <0.005 Co, and 1 to 10 Cr<sub>2</sub>O<sub>3</sub>. Acidic and basic slags are subjected to conversion of magnetic separation to remove trapped particles of ferronickel. Ferronickel is usually cast on conveyor machines in ingots of 25 to 35 kg weight. The specific energy consumption for processing 1 ton of dry lean nickel ore (1% Ni) is 810 kWh or 78 200 kWh per 1 ton of nickel. The use of richer ores (2.5% to 3.0% Ni) allows the decrease of specific energy consumption at least twofold (Novikov et al., 2005). The combined nickel yield into ferronickel is 88% to 93%.

Among alternative technologies of ferronickel smelting and refining, blowing molten iron and nickel ore mixture with reducing gas (Krasheninnikov and Leontiev, 2001) might be mentioned. The addition of 20% limestone allowed an increase of nickel content in the metal to 70%, in slag <0.1%, to achieve a nickel yield of 93%.

In the electric furnace development for ferronickel smelting, the trend is to go to higher-power furnaces (90 to 120 MVA), as the capital investment might decrease almost twice when compared to the cost of using low-power furnaces (Walker et al., 2010), but the operation of these furnaces also requires a proper turnover of materials and lower costs of electric energy.

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