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Advances and Innovations in Ferronickel-Making

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Preface

As an important strategic metal, nickel has found extensive application in stainless-steel industry and other fields. Electrolytic nickel is usually used as the feed for the traditional nickel-based stainless-steel production process. However, its production relies on the nickel sulfide ore resource which is gradually depleted. As the supply of nickel sulfide ore can no longer meet the demand of stainless-steel industry, other nickel ore resources, mainly laterite ore, are receiving increasing attentions in producing ferronickel which is now replacing electrolytic nickel as nickel source for the development of stainless-steel industry.

Over the past two decades, the global ferronickel industry has experienced a rapid expansion, as witnessed by the development of the rotary kiln-electric furnace (RKEF) smelting technology for ferronickel-making. Nevertheless, the RKEF process still faces a few intractable problems, such as huge energy consumption and massive discharge of ferronickel slag which causes head-scratching environmental pollution further endangering the survival of ferronickel industry. In China, there exist more rigorous challenges mainly due to the shortage of laterite ore that results in heavy dependence on importation in addition to the above problems. It is urgent to develop fresh processes, methods, and technologies for efficient and sustainable ferronickel-making.

In view of the above problems, the authors of this book and their research team have been wedded to innovating ferronickel-making for nearly twenty years from the aspects of development of new ferronickel production process, innovation of existing processes, value-added utilization of ferronickel slag, etc. For instance, they invented a process for preparing ferronickel from laterite ore by selective solid-state reduction-magnetic separation, allowing decrease of reduction temperature by 500 °C and cost saving of over 30% in comparison with the traditional RKEF process. They also developed a pioneering technology for regulating slag system of reductive smelting of laterite ore and a novel technology for controlling softening-melting performance of laterite ore, enabling decline of smelting temperature by 100 °C and electricity saving of 600 kWh per ton of ferronickel. Moreover, they proposed new methods for preparation of forsterite refractory materials and lightweight thermal insulation materials from ferronickel slag, realizing highly efficient value-added utilization

of the solid waste. These efforts point to a feasibility to solve the tough problems existing in the process of ferronickel-making. The authors are thus committed to sharing these advances through the present book with readers although it is clearly not comprehensive in its coverage of relevant information.

This book covers six chapters and is organized following the hierarchy of basic research, technological development, and industrial application. Chapter 1 introduces the basic properties and applications of nickel, laterite ore treatment, technological progress, existing problems, challenges, and development trend of ferronickel industry. Chapter 2 presents a novel ferronickel-making process via selective solid-state reduction-magnetic separation of laterite ore, featured by short process, high energy efficiency, and low cost, based on exploration of thermodynamic and kinetic laws of selective reduction and sulfidation of laterite ore with clarification of the growth behavior of ferronickel grains in the process of solid-state reductive roasting. With the much lower operating temperature in comparison with those in traditional ferronickel-making processes, it represents an exciting breakthrough in rational and optimal utilization of low- and medium-grade laterite ore resources for developing ferronickel and stainless-steel industry. Chapter 3 discusses the effects of calcium, magnesium, silicon, aluminum, and ferrous oxide on the properties of slag, from which a new low melting point slag type with diopside and mafic olivine as the main phases and a technology for slag system optimization and regulation centering on controlling FeO content and simultaneous adjustment of quaternary alkalinity are described with the purpose of reducing smelting temperature of electric arc furnace with less power consumption and higher metal recovery. Chapter 4 presents an original technical scheme of reducing the softening-melting temperature of laterite ore with promoted formation of liquid phase based on identification of the relationship between phase transformation and softening-melting property in the roasting process of laterite ore. It also clarifies the formation behavior of low melting point diopside phase during high-temperature roasting from which an innovative technology for regulating the softening-melting performance of laterite ore is presented. The findings denote efforts to improvement of the output and quality of laterite ore sinter and the smelting index of blast furnace, decrease of reduction temperature, acceleration of growth of ferronickel particles, and enhancement of separation of ferronickel in the Krupp–Renn process. Chapter 5 describes in detail the value-added utilization of ferronickel slag for preparing refractory materials and lightweight thermal insulation materials by comprehensively applying a series of techniques including biphasic design, particle gradation, and additive induction to optimize the phase composition, liquid phase generation, and volume/structure of product. Chapter 6 highlights a creative technical route of co-processing stainless-steel pickling sludge, which contains multiple valuable elements and sulfur that hinders its utilization and deteriorates the product quality when recycled as the feed for ferronickel production, with laterite ore via the RKEF process, based on analysis of desulfurization behaviors of the sludge, including thermodynamics, phase transformation, and off-gas emission characteristics during reduction.

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Tao Jiang

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Chapter 1

An Overview of Nickel Utilization from Laterite Ore



Abstract Ferronickel is an important alloy and intermediate product for manufacturing many advanced materials with versatile functions, e.g., stainless steel. Its properties and performance are mainly relied on the content of nickel, which is now primarily extracted from laterite ore. This chapter provides an overview of nickel utilization from laterite ore. Based on a brief introduction of properties of metallic nickel, it summarizes the applications of nickel, demand of nickel, resources of nickel, and metallurgical processes of laterite ore, in which the rotary kiln-electric furnace (RKEF) smelting process is dominant for production of ferronickel. Lastly, it discusses the challenges and development of ferronickel-making.

Keyword Nickel · Ferronickel-making · Laterite ores · Hydrometallurgical processes · Pyrometallurgical processes · RKEF

Nickel is a kind of silvery white ferromagnetic metal firstly separated by Swedish mineralogist A.F. Cronstedt in 1751. It is in the eighth group of the fourth period in the periodic table of elements, with atomic number of 28, atomic weight of 58.71, density of 8.9 g/cm^3 (20 °C), melting point of 1455 °C, and boiling point of 2915 °C. The most stable oxidation state of nickel is +2, but the oxidation valences of +1, +3 and +4 are also well known. The main oxides and sulfide compounds include NiO, Ni_3O_4 , Ni_2O_3 , NiS_2 , Ni_6S_5 , Ni_3S_2 , and NiS. In addition, NiO has a melting point of 1650–1660 °C. It is easily reduced to metallic nickel using carbon or carbon monoxide as reducing agent. Ni can react with CO to form $\text{Ni}(\text{CO})_4$, which is a colorless liquid with boiling point of 43 °C. $\text{Ni}(\text{CO})_4$ decomposes back to nickel and carbon monoxide upon heating to 180 °C.

Metallic nickel has good ductility and toughness, with an elongation of 25–45%. It can be pressed into thin sheets of less than 0.02 mm for forging and rolling various parts. Nickel has excellent oxidation and corrosion resistance performance. The dense oxide film formed on the surface of nickel would prevent its internal oxidation at normal temperature in humid atmosphere. Nickel can resist corrosions of fluorine, alkaline water, and organic substances and dissolve slowly in dilute acid. The surface of nickel is passivated in strong nitric acid solution, preventing further corrosion.

1.1 Applications of Nickel

Nickel is an indispensable metal in high-tech field. It is mainly used as an alloying element for production of stainless steel, high-temperature alloy steel, high-performance special alloy, and nickel-based plating materials (Fig. 1.1) [1]. Nickel can alloy readily with many other metals, including chromium, iron, copper, and cobalt. This allows for a wide variety of alloys that demonstrate outstanding resistance to corrosion and scaling, exceptional high-temperature strength, and other unique properties. For example, the copper-nickel alloys are featured by unique combination of strong resistance to corrosion, good thermal conductivity, and low macro-organism attachment in marine environments [2, 3]. They are applied in the fields of offshore oil and gas exploration, ship building, desalination, and power generation [4, 5]. The nickel–cobalt alloy is a kind of permanent magnetic material and is widely used in the field of electronic remote control, atomic energy industry and ultrasonic technology [6–8]. Besides, in chemical industry, nickel and its alloys are usually used as catalysts for hydrogenation reactions.

Nickel can also be used as anticorrosive coating on ceramic pigments and metal surfaces [9] and its demand proportion reached 7%. The nickel plating provides a unique combination of corrosion and wear resistances [10, 11]. It is used to increase brightness, lustre, appeal, and adhesion properties for subsequent coating layers.

Nickel foam and hydrogen storage metal, which are synthesized by nickel and rare earth, are widely used in the production of Ni–MH and Ni–Cd batteries due to the hydrogen absorption ability of nickel [12, 13]. More significantly, because of the increase of electric vehicles and the popularity of Ni-rich ternary cathode materials (e.g., NCM 811) for lithium batteries [14, 15], the nickel demand is expected to grow significantly [16]. The consumption of primary nickel in ternary Li-ion batteries was about 230 kilotons in 2021. This value is expected to reach 900 kilotons by 2030. The proportion of nickel demand for batteries is estimated to increase from 7% in 2021 to 35% by 2030, making batteries the second-largest application of nickel after stainless steel.

Fig. 1.1 Applications of primary nickel worldwide in various fields [1]

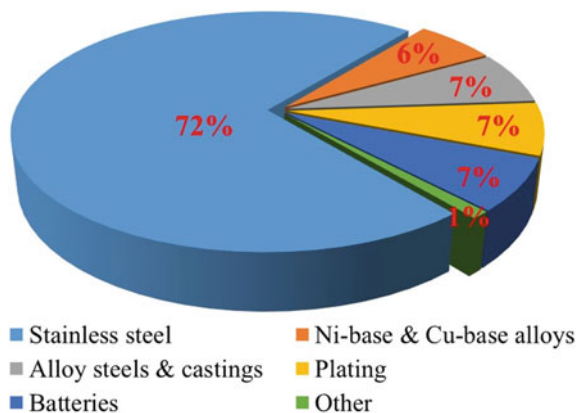


Table 1.1 Properties of various series of stainless steel

Classification	Crystalline structure	Magnetism	Corrosion resistance	Machinability
200 series	Austenite	No	Mediate	Good
300 series	Austenite	No	Excellent	Excellent
400 series	Ferrite/Martensite	Good	Good	Mediate

More than two thirds of global nickel production is used to produce stainless steel [17]. As an alloying element, nickel enhances steel properties such as formability, weldability and ductility, and corrosion resistance in certain applications [18]. It is widely used in civil products, building decoration and other industries. According to its main chemical composition, stainless steel can be divided into chromium stainless steel (400 series), chromium-nickel stainless steel (300 series), chromium manganese nitrogen stainless steel (200 series) [19, 20]. The main properties of various series of stainless steel are listed in Table 1.1.

Nickel promotes the formation of austenite and optimizes the crystal structure of steel, improving the plasticity, weldability, and toughness of stainless steel. The addition of nickel to plain carbon steel results in the transformation of crystal structure from body centered cubic (BCC) structure to face centered cubic structure (FCC), namely the austenitic structure. Except for nickel, carbon, nitrogen, manganese, and copper are also austenite-forming elements.

There are two opposite effects in stainless steel. Ferrite forming elements continuously form ferrite, while austenite forming elements incessantly form austenite. The final crystal structure of stainless steel depends on the relative quantity of these elements [21, 22]. There is a competitive relationship between chromium and austenite forming elements in the formation of crystal structure of stainless steel because chromium is a ferrite forming element. Therefore, the magnetic properties of 400 series stainless steel are good due to the fact that both iron and chromium are ferrite-forming elements. As the nickel content increases, the amount of austenite will gradually increase until all ferrite structures are transformed into austenite structures to form 300 series stainless steel. Duplex stainless steels have a mixed microstructure of austenite and ferrite in equal amount when the amount of nickel is decreased by half. At present, austenitic stainless steel accounts for 70% of stainless steel. The best-known types are type 304 with 8% nickel and type 316 with 11% nickel.

1.2 Demand of Nickel

The global production and consumption of primary nickel have increased continuously in the past decade. Figure 1.2 shows that the global consumption of primary nickel was 1.47 million tons in 2010 and increased to 2.93 million tons in 2021, with the growth rate of 100% [23, 24]. On the other hand, the production of nickel reached 1.44 million tons in 2010, reaching 2.79 million tons in 2021, with an increase of

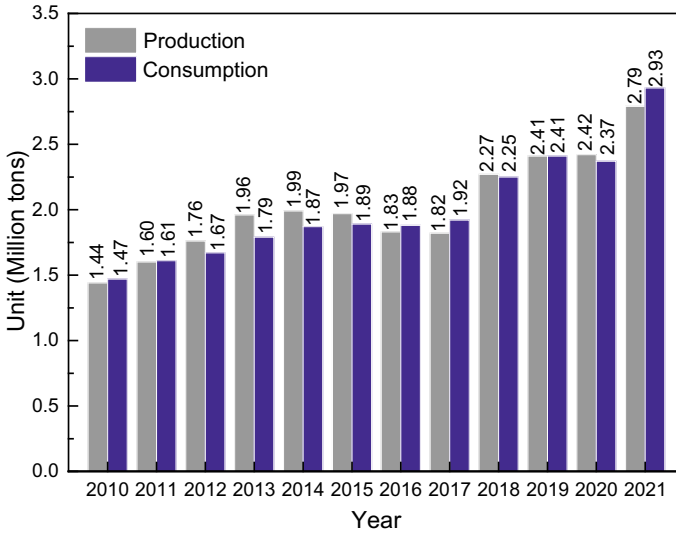


Fig. 1.2 Global production and consumption of primary nickel in 2010–2021

more than 93% from 2010. From 2015 to 2017, the annual output of primary nickel decreased slightly from 1.97 million tons to 1.82 million tons. The nickel production was higher than the consumption globally in 2012–2015, leading to the slight decreases of nickel production in 2016 and 2017.

The global consumption proportion of primary nickel is shown in Fig. 1.3. The countries with large proportions of nickel consumption include China (53%), America (8%), Japan (7%), South Korea (4%), Italy (4%), Germany (3%), and India (3%). Among them, the nickel consumption in China accounts for more than half of the global primary nickel consumption. It is mainly attributed to the rapid development of infrastructure construction, which consumes large amounts of stainless steel (Fig. 1.4). Apart from China, the countries with large nickel consumption are mainly developed countries. The developing countries consume little primary nickel. Evidently, the nickel demand and stainless steel consumption have a close correlation (Figs. 1.3 and 1.4). The global demand for primary nickel is expected to increase continuously considering economic development of developing countries with more investment in infrastructure.

As shown in Fig. 1.5, the nickel production gradually increased from 330 in 2010 to 736 thousand tons in 2013 in China, with an average annual growth rate of more than 40%. Since 2014, the nickel production in China has decreased due to the overseas investment of Chinese enterprises in the construction of ferronickel production lines. In recent years, the nickel consumption has shown an obvious growth trend in China. The nickel consumption was 590 thousand tons in 2010 and increased to 1542 thousand tons in 2021, with a growth rate of nearly 161%. The nickel output has been unable to meet the primary nickel demand for stainless steel

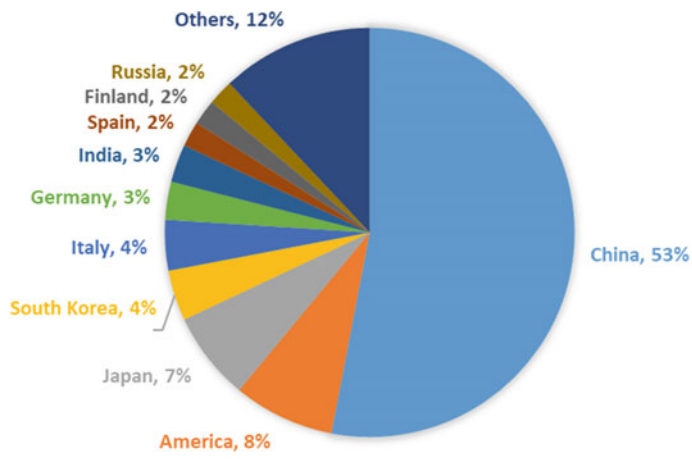


Fig. 1.3 Consumption proportion of crude nickel around the world

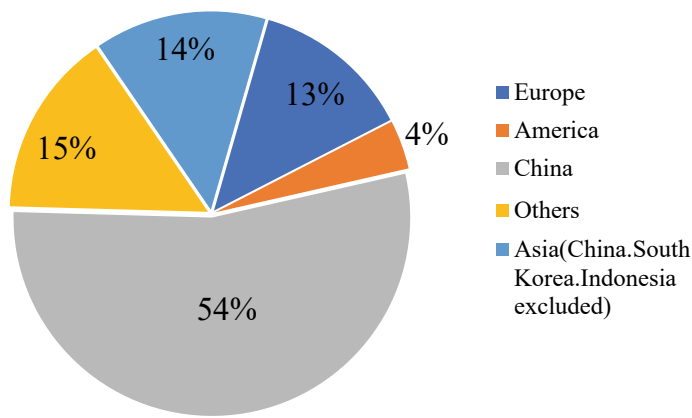


Fig. 1.4 Distribution of stainless steel production around the world in 2021

production. From 2010 to 2019, the average annual nickel import accounted for more than 30% of the primary nickel consumption. Especially, in 2021, the decline in domestic production brought the nickel import to 865 thousand tons, more than half of the domestic consumption that year. According to Figs. 1.2 and 1.5, the global nickel consumption from 2010 to 2017 maintained at approximately 900 thousand tons per year, except for China. Evidently, the demand of primary nickel in China drives the global nickel production and consumption.

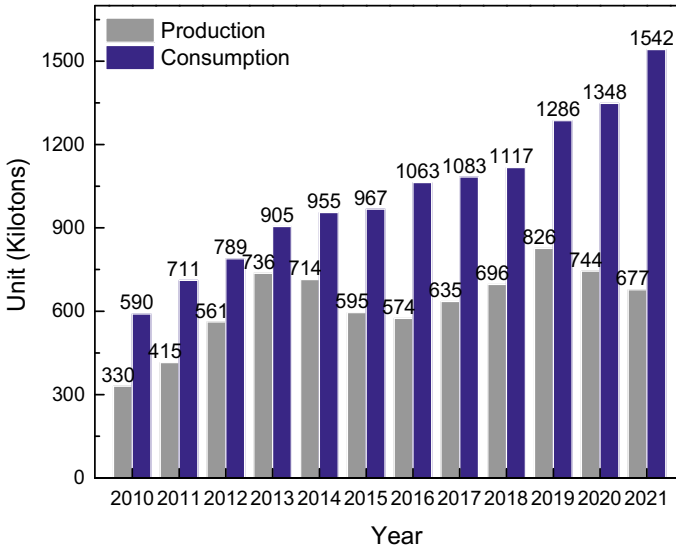


Fig. 1.5 Production and consumption of primary nickel in China in 2010–2021

1.3 Resources of Nickel

There are abundant nickel resources in the world. Nickel exists in the form of natural ferronickel alloy in the core of the earth but it cannot be extracted. The available nickel resources in the world include three main types, namely nickel sulfide ores, laterite ores, and submarine manganese nodules. Compared with nickel sulfide ores and laterite ores, the submarine manganese nodules have not been used effectively due to the limitation of mining technology and high cost. According to the statistics of the United States geological survey in 2021, the global proven land-based nickel reserves are about 96 million tons and the total nickel resources are approximately 130 million tons. They are mainly distributed in Australia, Brazil, New Caledonia, Russia, Cuba, Indonesia, South Africa, Philippines, China, and Canada (Fig. 1.6) [25]. Among them, the countries located near the equator have the most abundant nickel resources, particularly, laterite ores (Fig. 1.6). Indonesia and Australia have 21 and 19 million tons of nickel reserves, respectively, accounting for approximately 42% of the global reserves. The sum of nickel reserves in the top ten countries accounts for approximately 90% of the global reserves, indicating uneven distribution of nickel resources.

About 130 million tons of nickel resources with an average nickel content of 1% or more have been proved. Among these nickel resources, nickel sulfide ores account for about 40% and laterite ores account for about 60%. The former is mainly distributed in Canada, Russia, Australia, China and South Africa. Its deposit areas include the Kambalda nickel deposit in Australia, Kola peninsula and Siberia Norilsk nickel

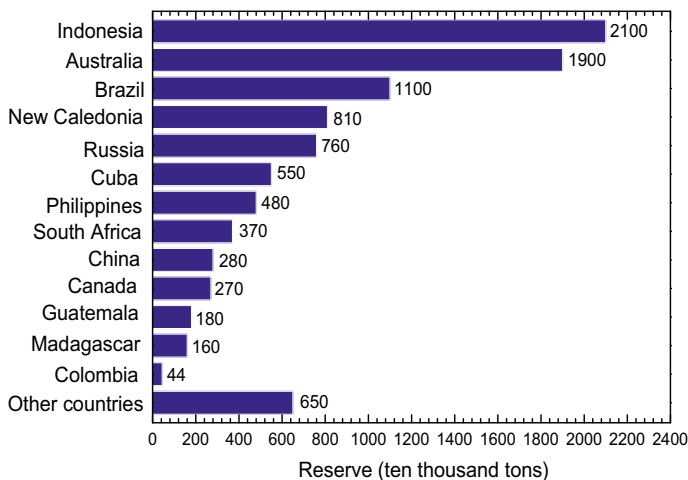


Fig. 1.6 Reserves of nickel resources in the world [25]

deposits in Russian, Sudbury, and Manitoba Thompson nickel deposits in Canada, and Jinchuan nickel and Panshi nickel deposits in China [26–28].

The laterite ores in the world are mainly distributed near the equator, including Indonesia, Brazil, New Caledonia, Cuba, Philippines, and Myanmar. Their large mines include New Caledonia nickel mines, Orient nickel mines in Cuba, Molucca and Sulawesi nickel mines in Indonesia, Palawan nickel mines in Philippines, Queensland nickel mines in Australia, Bannan nickel mines in Dominica, and Rajema nickel mines in Greece.

The reserves of nickel in China are 2.8 million tons, ranking ninth in the world (Fig. 1.6). By comparing the quantity of nickel resources with the consumption of crude nickel in recent years (Figs. 1.5 and 1.6), it is shown that the nickel reserves in China are unable to meet the long-term national demand, which is the main reason for its huge import of nickel resources and intermediate products, such as ferronickel and nickel sulfates. According to the distribution of nickel mineral resources, the sulfide nickel resources are abundant, and their quantity accounts for more than 90% of the total nickel resources in China. Gansu province of China has the largest nickel sulfide ores, accounting for about 62% of total nickel reserves. The main mining areas are Jinchuan mine, Kratonk mine and Huangshan mine. Jinchuan mine is rich in nickel, behind Sudbury mine in Canada, ranking second in the world.

On the other hand, the laterite ores in China are deficient and the amount of laterite ores only accounts for about 10% of the total resources. In China, there are still problems of low nickel grade and high mining cost in laterite deposits. Because of large stainless steel consumption, China needs to import a huge number of laterite ores from Indonesia, Australia, and Philippines every year to develop stainless steel production. China imported most of laterite ores from Indonesia before the country issued the policy of restricting the export of nickel ores in 2014. In recent years,

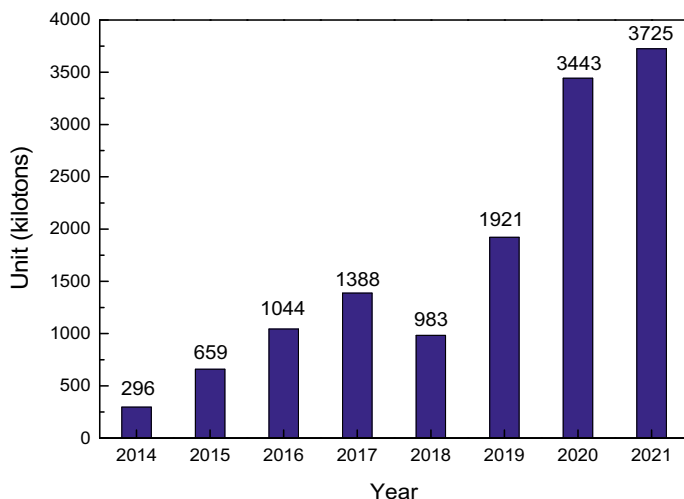


Fig. 1.7 Import of ferronickel in China since 2014–2021

a part of laterite ores has been imported from Philippines. Besides, many Chinese enterprises built ferronickel production plants in Indonesia. As a result, the amount of ferronickel imported from Indonesia has markedly increased since 2015. The import of ferronickel was only 296 kilotons in 2014, while this value increased to 1388 kilotons in 2017 (Fig. 1.7). After the Indonesian government relaxed the restrictions on the export of nickel resources again in 2017, the import of laterite ores from Indonesia was increased. Conversely, the import of ferronickel was decreased in 2018. Unfortunately, Indonesia issued the policy of restricting the export of laterite ores in 2019. The ferronickel imports reached the highest value of 3725 kilotons in 2021, with about 84% (3118 kilotons) from Indonesia.

1.4 Metallurgical Processes of Laterite Ore

Due to the limited treatment technology of laterite ores, sulfide ores were the main source of global nickel production for quite a long time in the past. High-grade sulfide ores were used as raw materials to produce high-quality nickel products. With gradual depletion of sulfide ores, it is difficult to meet increasing demand of raw materials. Thus, it is important to make full use of laterite ores with low cost. Compared with sulfide ores, laterite ores are more abundant and easier to be exploited. Many kinds of valuable metals, such as cobalt, iron, magnesium and chromium, are associated with laterite ores. The comprehensive recovery of these valuable metals can improve the utilization efficiency of the resources. In recent years, the development of laterite ores has made rapid progress. According to statistics, the amount of crude nickel

derived from laterite ores has surpassed the amount derived from sulfide ores in 2010, opening a new chapter for the use of laterite ores in nickel production [29].

Generally, laterite ore deposits can be divided into three different layers from top to bottom, namely, limonite layer, transition layer and saprolite layer [30, 31], as shown in Figs. 1.8 and 1.9. Due to long-term weathering and eluviation, the nickel grade of limonitic laterite ore is the lowest while the iron grade is the highest. Nickel mainly exists in goethite in the form of lattice substitution [32, 33]. The saprolite laterite ore has the highest nickel grade and lower iron grade. Iron mainly exists in the form of silicates, such as serpentine [34, 35]. The nickel and iron grades in the transition layer are between the limonite and saprolite layers and they mainly occur in goethite, hematite, and silicates.

The contents of cobalt, magnesium, silicon, aluminum, and chromium in laterite ore are also different (Fig. 1.9). The extraction and separation of these elements require different metallurgical methods. The limonitic laterite ore is relatively suitable for extracting valuable metals such as nickel and cobalt by hydrometallurgy due to its low contents of magnesium and silicon and high content of cobalt. However, the saprolitic laterite ore has high content of nickel and low content of iron and it is more suitable for ferronickel production using pyrometallurgical methods. For laterite ore in the transition layer, both pyrometallurgical and hydrometallurgical processes may meet the production requirements.

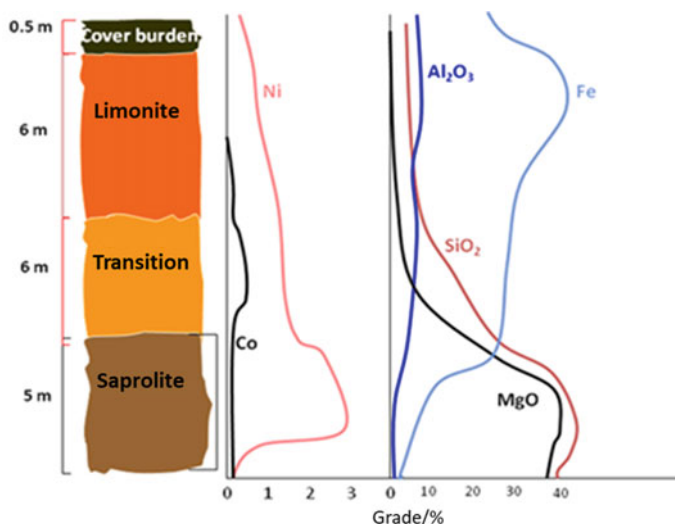


Fig. 1.8 Schematic illustration of distribution and chemical composition of laterite ore deposits

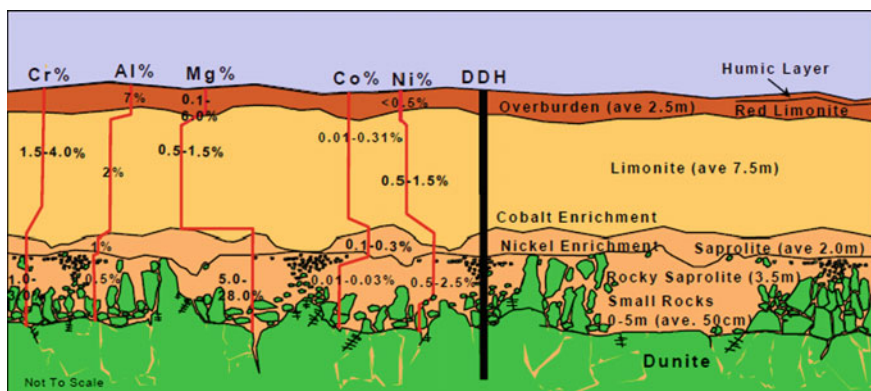
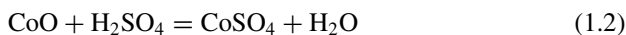
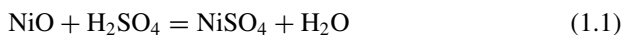


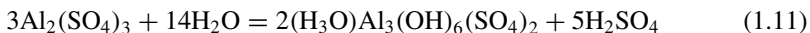
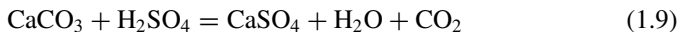
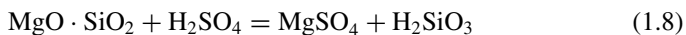
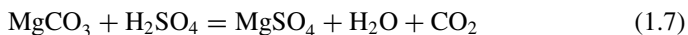
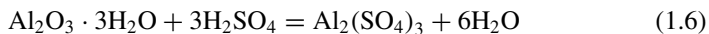
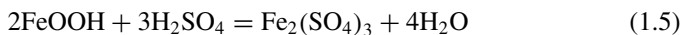
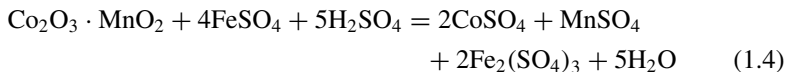
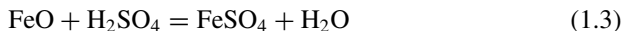
Fig. 1.9 Profile of the Remu laterite ore in the Papua New Guinea [31]

1.4.1 Hydrometallurgical Processes

1.4.1.1 High-Pressure Acid Leaching (HPAL) Process

The high-pressure acid leaching (HPAL) process of laterite ore was developed in the 1950s. The flowsheet of the HPAL process is shown in Fig. 1.10. The metal elements, including nickel, iron, and cobalt, are selectively leached at high temperature and high pressure. The leaching of nickel and cobalt reach nearly 95%, while most of the impurity components such as iron and aluminum retain in the leaching residue [36, 37]. The components are dissolved in sulphuric acid at leaching temperature of 245–265 °C and pressure of 4–5 MPa (Eqs. 1.1–1.9). The iron and aluminum ions in the solution are hydrolyzed at high temperature and pressure and then transformed into hematite and hydrated alunite (Eqs. 1.10 and 1.11), resulting in the selective leaching of nickel/cobalt over iron/aluminum [38–40]. A recent study reported that the leaching percentages of nickel and cobalt were 97% and 96%, respectively, while that of iron was less than 1%, with sulfuric acid concentration of 250 kg/t, liquid/solid ratio of 3 mL/g, leaching temperature of 250 °C, and leaching time of 1 h [41]. In addition, the leached silicon precipitated when it was cooled (Eq. 1.8). The remaining impurities such as iron and aluminum in the lixivium were precipitated and separated by adjusting pH value, while nickel, cobalt, and magnesium entered the leachate. When sulfidizing agents or alkalis were added, the sulfides or hydroxides were precipitated and the products (Ni, Co)(OH)₂ or (Ni, Co)S could be obtained.





The high-pressure acid leaching process of limonitic laterite ore has been successfully adopted by MOA (Cuba), Bulong, Cawse, Murrin Murrin and Ravensthorpe plants (Australia), Coral Bay and Taganito plants (Philippines), Ramu plant (Papua New Guinea), Ambatovy (Madagascar) and other enterprises [42–44]. It has some advantages in extracting nickel and cobalt from limonitic laterite ore, despite a few problems. At present, the process is mainly used to treat limonitic laterite ore with high iron content and low silicon and magnesium contents. Generally, the magnesium content is required to be less than 5%. The main reason is that high magnesium content in the raw material leads to large acid consumption and high cost of magnesium separation in the subsequent leaching solution [45, 46]. Due to the strict production conditions of high temperature, pressure and corrosion, the process needs special facilities (such as titanium alloy autoclave), greatly increasing the investment and production costs [36]. On the other hand, along with the generation of hematite, hydrated alunite, and calcium sulfate (Eqs. 1.9–1.11), scales are easily formed inside the autoclave during leaching [47]. Removing the scales needs to stop the autoclave, which affects the operation of the production. On the other hand, because of the high iron content in limonitic laterite ore, for every ton of nickel leached, over 100 tons of acidic iron-containing residues are generated in the HPAL plants. These residues are typically discharged into deep seas, causing marine pollution. In view of this fact, the tailings pond should be constructed in the new HAPL production lines.

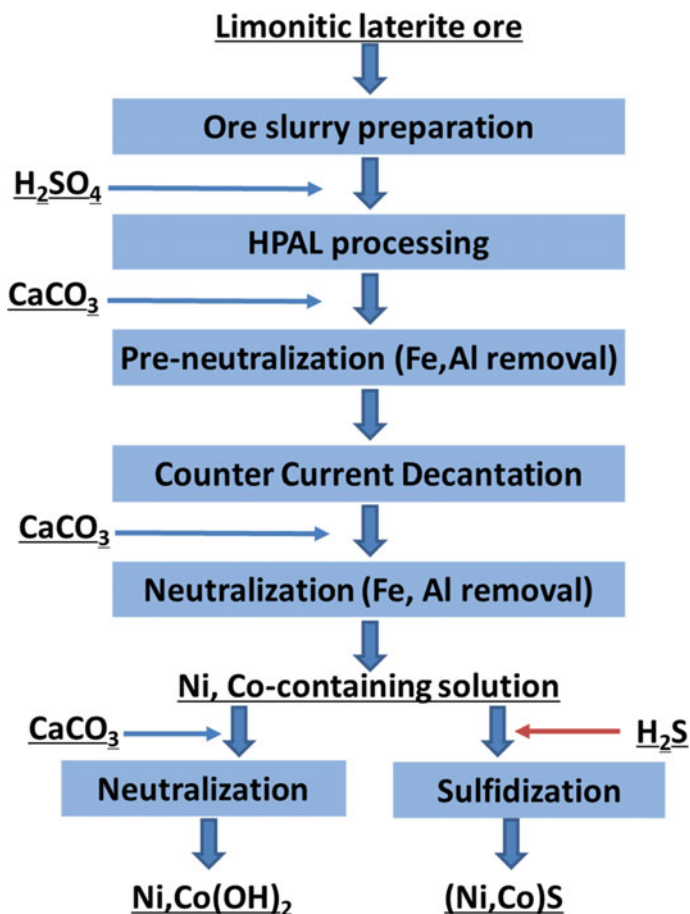
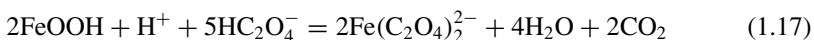
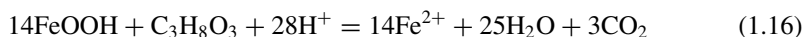
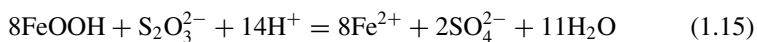
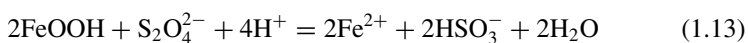


Fig. 1.10 Flowsheet of the HPAL process

1.4.1.2 Atmospheric Acid Leaching (AL) Process

In view of the shortcomings of the HPAL process, the technology of acid leaching at atmospheric pressure to treat limonitic laterite ore has attracted widespread attention [48]. Compared with HPAL, the atmospheric acid leaching (AL) process is simpler with advantages of lower energy consumption and less strict requirement for apparatuses [32, 49]. Hydrochloric acid, sulfuric acid, and nitric acid are commonly used in this process. However, since nickel mainly exists in the form of lattice substitution in the goethite, leaching of nickel depends on the dissolution of goethite [50, 51], which is difficult to dissolve under atmospheric condition, resulting in a low nickel leaching percentage (40–60%) [52, 53]. Moreover, the dissolved iron ions cannot form hematite precipitation under this condition, causing poor leaching selectivity of nickel over iron. The leaching ratio of Ni to Fe is close to 1 [32, 52].

Adding some reducing agents (such as thiosulfate, hydrosulfite, and SO_2) and acids (such as citric acid and oxalic acid) can strengthen the dissolution of goethite, promoting nickel leaching (Eqs. 1.12–1.17) [53–55]. It was found that the leaching percentages of iron and nickel in laterite ore increased from 45% to 85% with the sulfuric acid concentration of 0.72 M at leaching temperature of 90 °C for 6 h with the addition of 0.3 M SO_2 [52]. Besides, due to the strengthened leaching of Co-doped manganese oxides, Co leaching should also be promoted after adding the reducing agents (Eq. 1.18). However, because of the simultaneous increase in the amount of leached iron, the leaching of nickel and iron also kept a linear relationship, which had a negative impact on the separation of nickel and iron in the subsequent solution.



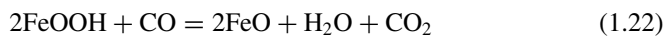
1.4.1.3 Combined HPAL-AL Leaching Process

The combined HPAL-AL leaching process is mainly applied to the treatment of limonitic and saprolitic laterite ores simultaneously [48]. Firstly, HPAL is used to treat the limonitic laterite ore and then the leachate is used for leaching saprolitic laterite ore at atmospheric pressure. The leaching residue derived from AL can be circulated for HPAL. The process utilizes the dissolution of magnesium-containing minerals in the saprolitic laterite to neutralize the excessive acid in the high-pressure leaching solution to adjust the pH value of the solution without adding other alkaline agents. Also, nickel and cobalt can be leached from saprolitic laterite ore using residual acid in high-pressure leaching solution, thereby improving the overall nickel recovery with lower production cost.

1.4.1.4 Reductive Roasting-Ammonia Leaching Process

To improve nickel leaching, some processes based on roasting followed by leaching have been developed [56–58]. They mainly include reductive roasting-ammonia leaching, reductive roasting-acid leaching, oxidative roasting-acid leaching, chlorinating roasting-water leaching, and sulfate roasting-water leaching.

Among these processes, the reductive roasting-ammonia leaching process (also known as the Caron process) has been used in industry. It has been applied in the Yabula refinery of QNI in Australia and the Nicaro smelter in Cuba [59, 60]. The laterite ore is selectively reduced at 600–700 °C. The nickel and cobalt oxides are reduced to the metallic state, while iron oxides are transformed into magnetite and wüstite (Eqs. 1.19–1.22). In addition, NH_3 and CO_2 are introduced into the leaching solution to leach the metallic nickel and cobalt in the form of ammoniac complex ion, while iron, magnesium and other impurities remain the leaching residue [61, 62]. However, in this process, the comprehensive recovery of nickel is about 75–80% and the recovery of cobalt is only 40–50%.



1.4.1.5 Reductive Roasting-Acid Leaching Process

The process of reductive roasting followed by acid leaching is similar to that of reductive roasting-ammonia leaching process, in which nickel and cobalt in laterite ore are selectively reduced to the metallic state by reduction, and hematite is reduced to magnetite and wüstite [63, 64]. Nickel and cobalt in the metallic state are easily dissolved in a diluted acid solution, increasing leaching of nickel and cobalt within shorter leaching time. A limonitic laterite ore (TFe 50.88 wt% and NiO 0.38 wt%) was reduced at 700 °C in the gas of 30 vol.% $\text{CO}/(\text{CO} + \text{CO}_2)$ for 90 min. The leaching percentage of nickel in the reduction product was 93% after leaching using 0.05 mol/L H_2SO_4 at temperature of 70 °C for 60 min [65]. The iron retained in the leaching residue was mainly in the form of magnetite, which could be used for iron-making after magnetic separation.

1.4.1.6 Oxidative Roasting-Acid Leaching Process

The oxidative roasting-acid leaching process is an alternative method. Its mechanism is different from that of the reductive roasting-acid leaching process. The goethite in laterite is dehydrated during roasting, and the specific surface area of the minerals is improved after roasting at 250–400 °C [63, 64]. The purpose of strengthening leaching of nickel and cobalt under the atmospheric pressure can be realized, depending on the change of the crystal structure and specific surface area of minerals [65, 66]. In the process of transformation from goethite to hematite (Eq. 1.23), the increase of activation energy of iron leaching leads to the decrease of iron leaching, eventually improving the selective leaching of nickel and cobalt. Compared with direct acid leaching, the leaching percentage of nickel increased from 67.1% to 92.7% while that of iron decreased from 78% to 32.5% after oxidative roasting at 400 °C, followed by leaching at 50 °C for 1 h with HCl concentration of 4 mol/L [67]. Garces-Granda et al. also reported an increase in the leaching percentage of nickel from 15.8% to 98.0% after roasting at 430 °C for 2 h (leaching temperature: 25 °C, time: 48 h, and HCl concentration: 3.2 M) [68]. However, due to uniform distribution of Ni in the structure of iron oxides, there was simultaneous dissolution of Ni and Fe.



1.4.1.7 Sulfatizing Roasting/Chloridizing Roasting-Water Leaching Process

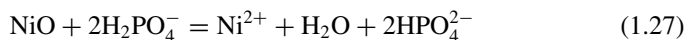
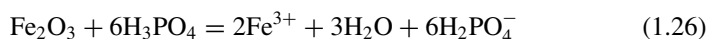
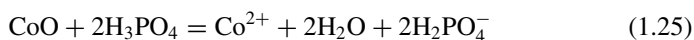
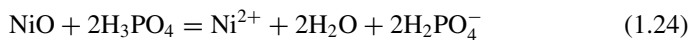
Through roasting with additives, the phase composition in laterite ores can be modified to improve their solubility in aqueous solution for higher leaching efficiency of nickel, cobalt, and other metals [69].

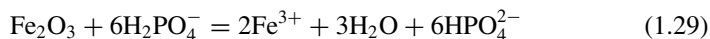
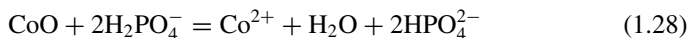
The principle of sulfatizing roasting-water leaching is basically the same as that of chloridizing roasting-water leaching. At certain temperature and atmosphere, the main metal components in laterite ores are transformed into water-soluble sulfate or chloride by using sulfur-containing or chlorine-containing additives. Concentrated sulfuric acid or sulfates (such as ammonium sulfate, ammonium bisulfate and sodium sulfate) are used as the additives in sulfatizing roasting in the temperature range 200–500 °C [70, 71]. Generally, chloride salts including sodium chloride and magnesium chloride are used in chloridizing roasting and its roasting temperature is higher than that of sulfatizing roasting, reaching about 700–1000 °C [72–74]. Li et al. used a mixture of NaCl and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as the additive for leaching of nickel, cobalt, and iron. Their leaching percentages were 87%, 58%, and 53%, respectively, after roasting at 900 °C, followed by water leaching [72]. The results showed that leaching of nickel and cobalt could be improved significantly. However, the leaching percentage of iron was also increased. In addition, the emission of hydrogen chloride gas during roasting would pose potential environmental risks.

1.4.1.8 Phosphoric Acid Leaching Process

As mentioned above, because of the high iron content in limonitic laterite ore, the selective leaching of nickel/cobalt over iron is a critical problem in hydrometallurgical processes. There are two feasible approaches: (i) limiting the dissolution of iron-bearing minerals and (ii) re-precipitation of the dissolved iron ions during leaching. In general, the limited dissolution of iron-bearing minerals results in a low leaching percentage of nickel, making it more feasible to re-precipitate the dissolved iron ions. In the above leaching processes, only the HPAL process can achieve re-precipitation of the dissolved iron ions and selective leaching of nickel and cobalt over iron. However, in this process, large amounts of acidic iron-containing residues are discharged into deep seas, causing marine pollution. The AL processes also produce large amounts of unutilized iron-residues while removing iron from lixivium by precipitation. This means that recovering iron components is important during the hydrometallurgical processing of laterite ore for cleaner production.

Recently, it was reported that phosphoric acid could be used as a leaching agent for processing limonitic laterite ore [75, 76]. Based on the differences in the solubility of phosphates, nickel and cobalt were leached (Eqs. 1.24–1.28) and iron phosphate was prepared simultaneously during leaching (Eqs. 1.29 and 1.30). This process could realize efficient leaching of nickel and cobalt, as well as a superior selective leaching of nickel and cobalt over iron. The related results showed that 98.7% of nickel and 89.8% of cobalt were leached from the roasted limonitic laterite ore (at 400 °C for 60 min) under the optimized leaching conditions (phosphoric acid concentration of 3 mol/L, leaching temperature of 90 °C, leaching time of 180 min, and liquid/solid ratio of 10 mL/g). Meanwhile, 98.3% of iron was converted into insoluble $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ [75]. By using another similar approach to with phosphoric acid, the leaching percentages of Ni, Co, and Fe were 99.2%, 81.8%, and 0.54%, respectively, in a 3 mol/L H_3PO_4 liquor at 130 °C for 2 h [76]. Compared with high-pressure leaching, the temperature required was decreased by 115–125 °C and the hydrothermal pressure was only 0.2–0.27 MPa. Furthermore, because of the simultaneous precipitations of Fe^{3+} and Al^{3+} , a lamellar Al-doped iron phosphate, $(\text{FePO}_4 \cdot 2\text{H}_2\text{O})$, as leaching precipitate was obtained at the (Fe + Al)/P molar ratio of 1.0 and purity of 99%, which could be used as the anode material for LiFePO_4 batteries after removing impurities. The process eliminated the generation of acidic residues and realized value-added utilization of iron in limonitic laterite ore.





1.4.1.9 Microbiological Leaching

The aim of microbiological or biological leaching process is to use the oxidation or reduction functions of microorganisms to oxidize or reduce certain mineral components in laterite ores to achieve the purpose of separating valuable components (Eq. 1.31) [77–79]. The components are oxidized or reduced, depending on the characteristics of microorganisms to achieve selective separation in the process. Compared with the HPAL and AL leaching processes, the use of biological leaching at room temperature takes longer time, even several months.



1.4.2 Pyrometallurgical Processes

Although a lot of studies of hydrometallurgical processes have been carried out for processing of laterite ores with low energy consumption, the hydrometallurgical technology is used in only a small proportion of enterprises for crude nickel production due to its limited scale and long production process. In contrast, pyrometallurgy can meet the demand of stainless steel industry for nickel through large-scale industrial production. At present, more than 70% of the global nickel production is based on pyrometallurgy, including the matte smelting process, rotary kiln reduction process, blast furnace smelting process and rotary kiln-electric furnace smelting process.

1.4.2.1 Matte Smelting Process

The nickel matte smelting process has been applied since 1920s and it was the first pyrometallurgical process of laterite ore in industrial production [80, 81]. By adding sulfur, sulfide ore or gypsum into laterite ore, the low-grade nickel matte ($\text{Ni}_3\text{S}_2 \cdot \text{FeS}$) is generated when the smelting process is carried out at 1500–1600 °C in blast furnace or electric arc furnace. Then, the high nickel matte with nickel grade more than 40%

is produced by converter blowing. The quantity of nickel matte produced by laterite ores is about 120 kilotons per year in the world (calculated by metal nickel).

The basic principle of nickel matte smelting is that the ore melts into liquid phase and the metal components including Ni, Co, and Fe react with sulfiding agents after reduction, forming mixed melt of nickel, cobalt, and iron sulfides, also named low-grade nickel matte [82]. The advantages of this process are simple equipment, mature technology, and adjustable products. After roasting and desulfuration, high-grade nickel matte can be used for direct reduction and preparation of crude nickel for stainless steel production. It can also be used as a feed for refining nickel by the atmospheric carbonyl method to produce nickel pellets and nickel powder. In addition, the matte can be made into anode plate to produce cathode nickel by electrolytic refining. However, there are also some problems in the matte smelting process, such as high energy consumption, heavy pollution, and poor nickel recovery (about 70% in the whole process). At present, the main factories that use this process are Anbo smelter in New Caledonia and Thorocco smelter in Sulawesi, Indonesia.

1.4.2.2 Rotary Kiln Reduction-Physical Separation Process

The laterite ore is dried, crushed, screened, and then mixed with flux and reducing agent in a certain proportion to form agglomerates. The agglomerates are dried and reduced in a rotary kiln. The calcines are then cooled by water quenching, crushed, and screened for magnetic or gravity separation to obtain ferronickel nuggets or powders [83, 84]. The whole process in the rotary kiln could be divided into three stages, including the drying stage, reduction stage, and growth stage of ferronickel particles, as shown in Fig. 1.11. The temperature of drying is generally lower than 800 °C, leading to the evaporation of the crystal water in the feeds. The reduction of nickel oxides and iron oxides take place in the reduction stage at 800–1250 °C. The ferronickel particles generated in the reduction stage are fully aggregated and remain in the molten or semi molten state at 1250–1450 °C [85–87].

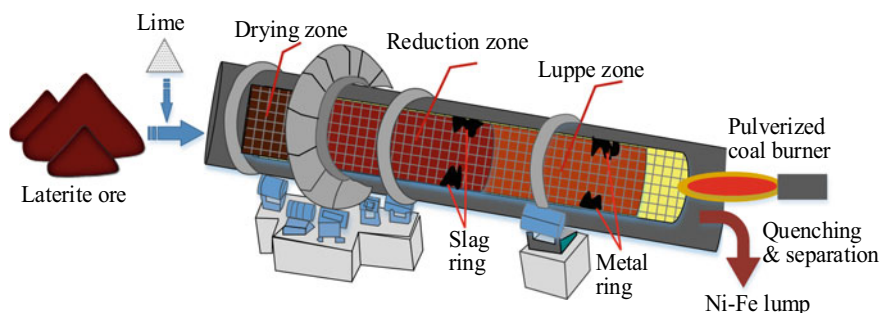


Fig. 1.11 Flowsheet of the rotary kiln reduction-physical separation process

The ferronickel production by the rotary kiln reduction-physical separation process has the advantages of short process and low energy consumption, mainly due to the use of coal as both heat source and reductant. About 80–85% of the total energy consumption is provided by coal. It is the most economical way to deal with high-grade saprolitic laterite ore. This process was originally developed from the Krupp-Renn process for ironmaking in Germany. In 1930s, Nippon Yakin Kogyo Co. Ltd. in Japan firstly used this process to produce ferronickel from laterite ores and is still running [88, 89]. The company is equipped with five rotary kiln production lines, which use high-grade laterite ore (more than 2 wt% Ni), limestone as desulfurizer, and anthracite as reducing agent. The annual output of ferronickel is about 15–20 kilotons (calculated by nickel metal).

Due to the obvious advantages of rotary kiln reduction-physical separation process, many ferronickel plants in China are developing or have already put into production of rotary kiln lines. Chaoyang Heavy Building Materials Machinery Manufacturing Co., Ltd. has successively carried out the tests and production of ferronickel in rotary kilns in Qiqihar and Jiangsu province, obtaining ferronickel products containing more than 10% of nickel. In 2013, Chengde Nickel Industry Co. Ltd. established four rotary kiln lines in Guangxi province. Desheng Stainless Steel Co. Ltd. of Baosteel group carried out the technical transformation project of direct reduction of ferronickel by rotary kiln in Fujian Luoyuan No. 2 Crude Refinery and the trial production was carried out in 2016. The overall nickel recovery could reach 90%. Shanghai Pan-Pacific Group has built two production lines in North Maluku province to produce ferronickel products (nickel grade: 10–13%). The second stage of Dafeng Port (Indonesia) of Heshun Nickel Industry Co., Ltd. plans to build six rotary kiln reduction lines in Sulawesi, Indonesia, which is expected to produce 150 kilotons of ferronickel per year.

1.4.2.3 Blast Furnace (BF) Smelting Process

The technological process of producing nickel pig iron (NPI) by smelting laterite ore in blast furnace is basically the same as that of modern BF smelting for producing pig iron from iron ores [29], as shown in Fig. 1.12. Initially, the laterite ore is crushed, mixed with flux and fuel, and then sintered in a sintering machine. The resulting sinter is smelted in BF to produce NPI. The process is usually applied for treatment of high iron and low magnesium limonitic laterite ore (nickel grade of 0.7–1.2 wt%) and the nickel grade of NPI is kept at 1–3 wt% to produce 200 series stainless steel. At the beginning of the twenty-first century, many private enterprises in China started to use small-scale BF (50–150 m³) to produce NPI [34, 35]. Due to the rapid increase of stainless steel demand in the early 2010s, this process has been developed in China. It turned into a typical NPI production process with Chinese characteristics.

Due to the restrictions of Chinese government policy, the small-scale BF has been shut down gradually in recent years. However, because the blast furnace smelting process has the advantages of mature technology, large production capacity, and low requirements for raw materials, some ferronickel plants still use this process

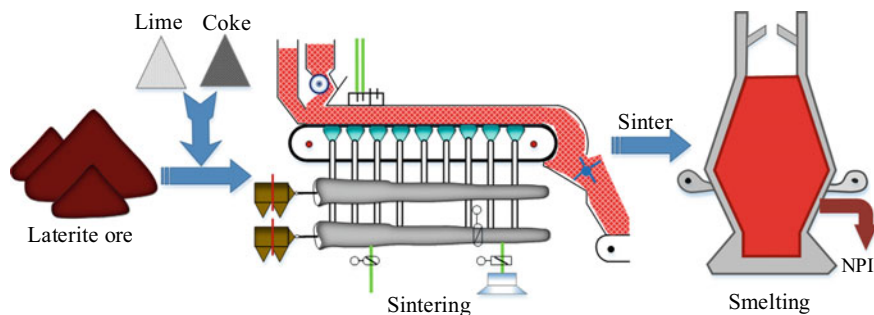


Fig. 1.12 Flowsheet of the blast furnace smelting process

to produce NPI for 200 series stainless steel. The capacity of new BF's in China is generally 350–600 m³. For example, Chengde Nickel Industry Co. Ltd. has three blast furnaces with capacity of 550 m³. Xinhai Technology Co., Ltd. operates a BF with capacity of 350 m³. Guangdong Guangqing Metal Technology Co. Ltd. and Fujian Qingtuo nickel industry Co. Ltd. have built a BF with capacity of 550 m³, respectively.

In addition, a few China-invested enterprises have built smaller BF's (about 80–150 m³) in Indonesia. Zhenshi Holding Group Co., Ltd. have been built four BF's with a volume of 80 m³ in Maluku to produce NPI with nickel grade below 10 wt%. In 2015, Lianfuda (Xiamen) Import and Export Co., Ltd. built three 80 m³ BF's in Indonesia, with an annual output of 1.8 kilotons of NPI (calculated by nickel). Ningbo Minghui Company and Hentyuan Metallurgy Company built a 128 m³ BF in Sulawesi and Banten provinces of Indonesia, respectively. New Hulian Group plans to build four BF line with capacity of 80 m³, with estimated annual output of 100 kilotons of NPI. Dafeng Port (Indonesia) Heshun Nickel Industry Co., Ltd. has built four BF's with capacity of 86 m³ in Sulawesi, Indonesia, with the annual output of 135–150 kilotons. In addition, some BF lines are planned or under construction in Indonesia by Qingdao Hengshun Zhongsheng Co., Ltd., Taizhou Yongxing Alloy Material Technology Co. Ltd., Fujian Fanhua Mining Co. Ltd., Ningxia Huayuan Metallurgical Industry Co., Ltd., Ningbo Yinyi Mining Co., Ltd., etc. Owing to the production of these BF's, China's imports of NPI from Indonesia have increased significantly in recent years.

1.4.2.4 Rotary Kiln-Electric Furnace (RKEF) Smelting Process

The rotary kiln-electric furnace (RKEF) smelting process was developed by Aiken Industries Inc. and applied in New Caledonia Doniambo smelter in the 1950s. Now it has become the mainstream process of producing ferronickel from laterite ores in the world [90, 91]. Its production capacity accounts for more than two-thirds of the global ferronickel production capacity. The flowsheet of this process is shown in Fig. 1.13. Due to high water content of laterite ores (about 30–40%), it is necessary

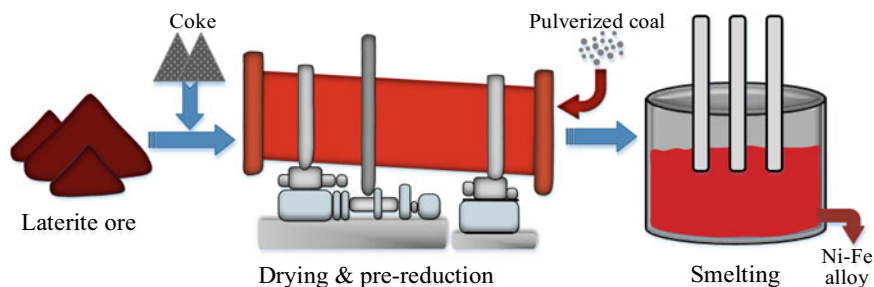


Fig. 1.13 Flowsheet of the rotary kiln-electric furnace smelting process

to dry the ore in advance. The dried laterite ore is reduced in a rotary kiln and the calcine is further smelted in the electric arc furnace to produce crude ferronickel alloy [17, 91]. The reductive roasting in rotary kiln can provide hot feeds for electric arc furnace smelting to save power consumption. On the other hand, a part of nickel and iron oxides in laterite ores are reduced to metallic state, decreasing smelting load of electric arc furnace. The flue gas from rotary kiln in the reduction process can be recycled to dry laterite ore. After purification, the CO-containing waste gas derived from electric arc furnace can also be used as reducing agent in rotary kiln.

The RKEF process has strong adaptability of raw materials and all kinds of laterite ores can be used for production. The quality of ferronickel products is excellent and the nickel content generally reaches 10–30 wt%, which can be used to produce 300 series stainless steel [92, 93]. At present, there are many enterprises using the RKEF process, such as Doniambo refinery of Eramet nickel group in New Caledonia, Hyuga smelter of Sumitomo Metal Mining Co., Ltd. (SMM), Tsuruga smelter of Nippon Mining & Metals Co., Ltd., SNNC smelter of South Korea's POSCO, Onsan refinery of Korea Nickel Corp., Soroako smelter of International Nickel Corp. (INCO), and Pomaala smelter of PT. Aneka Tambang.

At the beginning of 2010, ENFI Engineering Corp. introduced the RKEF process and built a ferronickel production line in China. The Chinese government has explicitly listed “the RKEF technology for producing ferronickel from laterite ore” as an encouraged industry in the Guiding Catalogue of Industrial Structure Adjustment (2011 edition). This process has made great progress in China. Since then, most of the new ferronickel plants and ferronickel production lines have adopted this process. Due to restrictions on imported laterite ores, the nickel content in ferronickel generally reaches 10–15 wt%. Shandong Xinhai Technology Co., Ltd. and Jiangsu Delong Nickel Industry Co., Ltd. have built 30 RKEF lines and 20 RKEF lines, respectively, with the production capacity of 1.8 million and 1.0 million tons of ferronickel. Based on the traditional RKEF process, Tsingshan Holding group has developed an integrated continuous casting and rolling process to produce ferronickel and downstream stainless steel. The new smelting process was applied in Fujian Dingxin Industrial Co., Ltd., and Guangdong Guangqing Metal Technology Co. Ltd. The

production costs of ferronickel and stainless steel have been significantly reduced, and the economic benefit has been significantly improved.

In addition to the ferronickel smelting projects already in production, there are some large-scale RKEF lines under construction in China. Jinchuan Group has designed an annual output of 1 million tons of ferronickel project in Guangxi province. Tangshan Kaiyuan industry Co., Ltd. designed an annual output of 1 million tons of ferronickel project. Linyi Yichen Ni–Cr Alloy Co. Ltd. plans to construct six RKEF lines, with an estimated output of 1 million tons of ferronickel per year. These enterprises generally use laterite ores imported from Philippines, Indonesia, and Myanmar.

Due to the export restrictions of laterite ores from Indonesia and the high cost of raw materials transportation, the ferronickel production enterprises began to build production lines in the origin of laterite ores in recent years. The electric arc furnace with capacity of 72,000 KWA of Tagaung Taung RKEF project designed by ENFI and invested by China Nonferrous Metals Group was put into operation in 2015. Tsingshan Holding group will put 52 RKEF lines into operation with capacity of 42 MWA in Indonesia and the ferronickel output will reach 4.0 million tons per year. Jiangsu Delong Nickel Industry Co., Ltd. will put 102 RKEF lines with capacity of 33 MWA into operation in Indonesia. The ferronickel output will reach 6.0 million tons per year. Xinxing Ductile Iron Pipes Co., Ltd. launched the RKEF project with an annual output of 190 kilotons ferronickel in Maluku and the total planned output will reach 760 kilotons. Jinchuan Group Co. Ltd. built 4 RKEF lines in Maluku with the output of 300 kilotons ferronickel in 2019. Macrolink group constructed the RKEF project with an annual output of 100 kilotons ferronickel. Besides, the enterprises including Qingdao Hengshun Zhongsheng Co., Ltd., Jiangsu Mingzhu International Trade Co. Ltd., Hanking Industrial Group Co., Ltd., Jiangsu Dafeng Haigang Holding Ltd., and E United Group have put RKEF lines into operation or plan to initiate similar projects in Indonesia. By the end of 2020, the output of the ferronickel smelting project constructed by Chinese enterprises in Indonesia reached nearly 5 million tons per year. The capacity under construction reaches 7–10 million tons of ferronickel per year, and the total capacity will be more than 12 million tons per year. The RKEF process of laterite ores is expected to have better development.

1.5 Challenges and Development of Ferronickel-Making

Stainless steel is an important material in the national economic construction. The global production of stainless steel increased from 31.09 million tons in 2010 to 56.29 million tons in 2021 (Fig. 1.14) and its output will maintain a growth trend in the future [17, 94]. The production and consumption of stainless steel in China have ranked first in the world for many years. Since 2014, the output of stainless steel in China was more than half of global output. As shown in Fig. 1.15, the output of stainless steel reached 30.63 million tons in 2021 and the consumption was

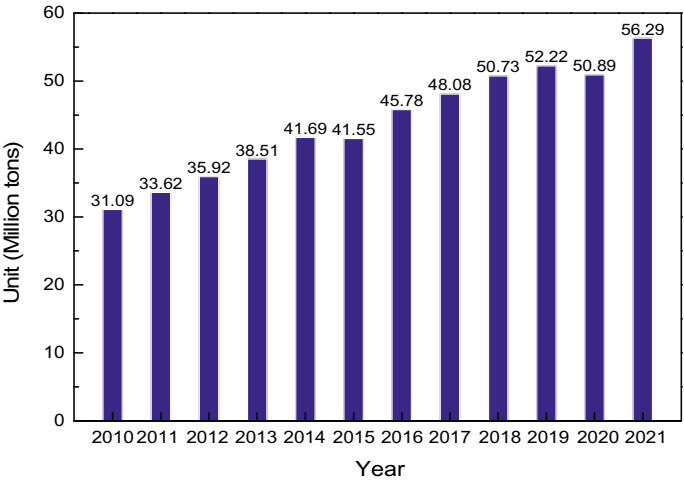


Fig. 1.14 Global output of stainless steel in 2010–2021

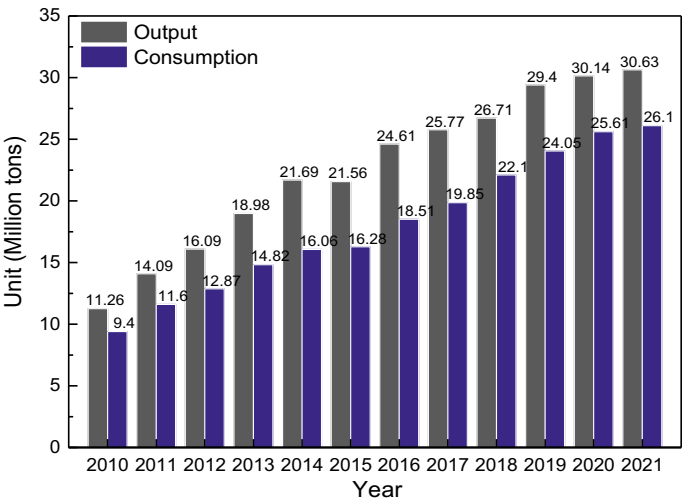
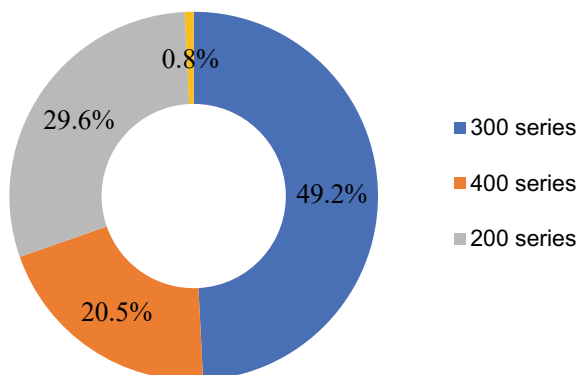


Fig. 1.15 Production and consumption of stainless steel in China in 2010–2021

26.1 million tons. Compared with the output and consumption in 2010, their growth rates were about 172% and 178%, respectively.

Nickel is mainly used in stainless steel production. The proportion of Ni-based stainless steel (including 200 series and 300 series) reached 80% in China in 2021 (Fig. 1.16). Traditional stainless steel production usually uses expensive electrolytic nickel as feed and its cost accounts for about 70% of the total cost of stainless steel production. As the price of ferronickel is much lower than that of electrolytic nickel,

Fig. 1.16 Distribution of various types of stainless steel in China in 2021



stainless steel enterprises gradually use ferronickel instead of electrolytic nickel. The addition of ferronickel is more than 60% during the stainless steel production in the Taiyuan Iron & Steel Co. Ltd. (TISCO) and China Baowu Steel Group Co., Ltd. The utilization percentage of ferronickel in the Tsingshan Holding Group is more than 90%. In 2010, the production and consumption of ferronickel exceeded those of electrolytic nickel, becoming the main source of crude nickel for stainless steel production. Laterite ores will be the main raw material of nickel production in the future. However, there are still some problems to be solved in the pyrometallurgical processes for ferronickel production, due to the special physical and chemical properties of laterite ores.

For the Krupp-Renn process, it is necessary to keep laterite ores in molten or semi-molten state to improve the mass transfer conditions inside the agglomerated feeds. This measure can promote aggregation and growth of ferronickel particles and realize the effective separation of ferronickel from slag in the physical separation process. However, the abundant silicon and magnesium components in saprolitic laterite ores form pyroxene and olivine with high melting points in the reduction process. In order to meet the formation conditions of liquid phase, the rotary kiln needs high roasting temperature and harsh operation conditions. In the reductive roasting process operated by the Nippon Yakin Kogyo Co., Ltd., serpentine in laterite ore will be transformed into forsterite, which requires increase of reduction temperature in the kiln head to 1400–1450 °C. On the other hand, it is difficult to control the amount of liquid phase in the reduction process, which leads to the formation of kiln-ring in the reduction zone and luppe zone [95, 96] (Fig. 1.11), inhibiting production. The above reasons limit its widespread application. Except the Nippon Yakin Kogyo Co., Ltd. which realizes the ferronickel production, other direct reduction lines such as the Chengde Nickel Industry Co. Ltd. and Desheng Stainless Steel Co., Ltd. of Baosteel group only use rotary kiln to reduce laterite ores within the temperature range 1200–1350 °C. About 65% of non-magnetic residue is separated by grinding and magnetic separation. The nickel-containing magnetic concentrate is then supplied to the electric arc furnace or BF for ferronickel smelting.

For blast furnace smelting process, the operation conditions of sintering and smelting are not the same as those of blast furnace smelting for iron-making, due to the difference between laterite ores and iron ores. In the sintering process of laterite ores, there exist many problems, such as high solid fuel consumption, high ratio of return fine, low ISO tumbling index and unsatisfactory size distribution of sinter [34, 35]. The large volume of slag and the low temperature of molten iron in BF cause difficult separation of slag and iron, due to the low grade of iron in laterite ores. Especially in the smelting of saprolitic laterite ore with low iron content (15–30 wt% TFe) and high magnesium (15–25 wt% MgO) content, the huge amount of smelting slag and the unsatisfied viscosity of the slag cause difficult production. This is also the main reason that the limonitic laterite ore with the high iron content (45–50 wt% TFe) and low magnesium (1–5 wt% MgO) content is generally used in the BF smelting process to produce low nickel-grade NPI. Besides, in order to ensure stable operation of BF, it is necessary to add a large amount of coke to elevate the smelting temperature. Generally, fluorite is added to improve the fluidity of molten slag and to strengthen the separation of molten iron from slag. As a result, there exists potential environmental pollution.

The biggest disadvantage of the RKEF process is the high energy consumption during smelting [17]. The cost proportion of electric power accounts for 21.40% of total production cost in the typical RKEF plants in China (Fig. 1.17). This proportion will be higher in Indonesia, due to the low cost of laterite ores. It is also associated with the large amount of slag discharged in the smelting of laterite ores and the requirement of high smelting temperature. In order to separate molten ferronickel from slag, the slag temperature generally needs to be maintained nearly 1600 °C, resulting in the energy consumption of 14 GJ/t-ferronickel during smelting [17, 97]. Several plants

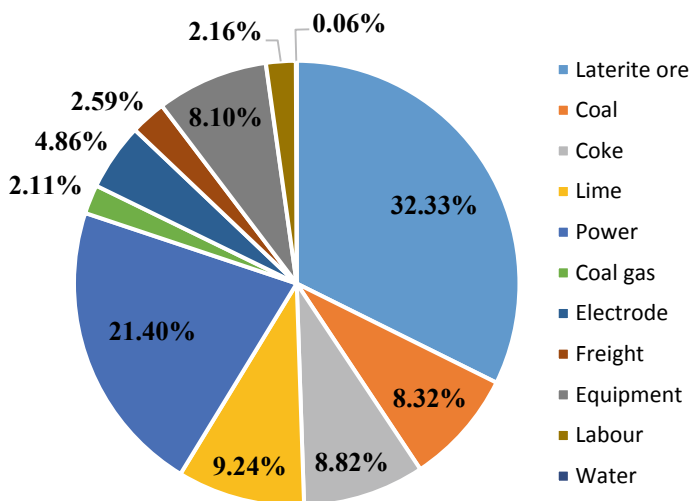


Fig. 1.17 Cost distribution of ferronickel production using the RKEF process in China

have tried to improve the production process to reduce energy consumption and cost based on the experience, such as controlling the MgO/SiO_2 mass ratio of feeds to reduce the smelting temperature, introducing the hot reduction calcine into electric arc furnace, recycling the waste heat of rotary kiln and the furnace gas for drying and reduction of laterite ore, and integrating the continuous casting and rolling process to ferronickel and stainless steel production [98, 99]. However, compared with the direct reduction process and blast furnace process, the cost of RKEF process is still 10–20% higher.

To sum up, although the process of smelting ferronickel from laterite ores in the world has developed rapidly in recent years, the problems such as frequent changes of raw materials, poor applicability of the process, long production process, large energy consumption and heavy environmental pollution still restrain the sustainable and healthy development of nickel industry and even stainless steel industry. It is urgent to carry out more in-depth research to break through technical bottlenecks in the production of ferronickel from laterite ores, realizing the low-cost, high-efficiency, and eco-friendly ferronickel production for better development of stainless steel industry.

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Chapter 2

Fundamentals of Selective Solid-State Reduction and Novel Process for Preparing Ferronickel from Laterite Ore



Abstract Due to the shortage of laterite ore resources in China, most of the raw nickeliferous materials for ferronickel production have to be imported. The low Ni grade (1–2 wt%), high water content (35–45 wt%) and high transportation cost of laterite ore result in costly production of ferronickel and stainless steel in China. This chapter presents a new method for preparing ferronickel from laterite ore based on selective solid-state reduction followed by magnetic separation. The key issues in the selective reduction of nickel oxides over iron oxides and the growth of newly-formed ferronickel grains (particles) were primarily discussed, and the related fundamentals such as thermodynamics, reduction/sulfidation behaviors of nickel and iron oxides in the ore as well as the growth of ferronickel particles during solid-state reduction were investigated. The pilot-scale tests and industrial tests were then conducted to validate the feasibility of the proposed new process.

Keyword Ferronickel · Selective reduction · Solid-state roasting · Magnetic separation · Sulfidation

2.1 Thermodynamics of Reduction/Sulfidation of Nickel and Iron Oxides

Due to the complicated reduction procedures of laterite ore and mutual influences of multiple reactions, the thermodynamic analysis will be useful for understanding the direction and limitation of each reaction in the process of reductive roasting and influence of reaction conditions on phase transformation of the ore. They will provide thermodynamic bases for the selective reduction of metal oxides.

From the thermodynamic perspective, if the standard Gibbs free energy change of reaction $\Delta_r G_m^\ominus = 0$, the reaction reaches the equilibrium state. When $\Delta_r G_m^\ominus < 0$, the reaction will proceed spontaneously in the forward direction. Conversely, when $\Delta_r G_m^\ominus > 0$, the reaction will proceed reversely. According to the equation $\Delta_r G_m = \Delta_r G_m^\ominus + RT \ln K$ in which R is the universal gas constant and T is the absolute temperature, when the reaction reaches equilibrium, i.e., $\Delta_r G_m^\ominus = 0$, the following equation can be obtained:

$$\ln K^{\ominus} = -\Delta_r G_m^{\ominus} / RT \quad (2.1)$$

$$\text{MeO} + \text{CO} = \text{Me} + \text{CO}_2, \quad \Delta_r G_m = A + BT \quad (2.2)$$

For reduction of metallic oxides (Eq. 2.2), when MeO and Me are pure condensed phases (i.e., activity $\alpha_{\text{Me}} = \alpha_{\text{MeO}} = 1$) and the system pressure has no influence on equilibrium of reaction, the number of degree of freedom of reaction is 1. Only temperature and gas composition affect equilibrium of reaction, so the equilibrium constant is:

$$K^{\ominus} = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{\text{CO}_2 \text{ vol}\%}{\text{CO vol}\%} \quad (2.3)$$

The correlation between equilibrium gas phase composition and temperature is expressed as follows:

$$\begin{aligned} \Delta_r G_m^{\ominus} = A + BT &= -RT \ln \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = -RT \ln \frac{\text{CO}_2 \text{ vol}\%}{\text{CO vol}\%} \\ \ln \frac{\% \text{CO}_2}{\% \text{CO}} &= -\frac{A + BT}{8.314T} = \frac{A'}{T} + B' \end{aligned} \quad (2.4)$$

Meanwhile,

$$\text{CO vol}\% + \text{CO}_2 \text{ vol}\% = 100\% \quad (2.5)$$

If MeO is given, one can calculate A' and B' and correlation between %CO and T based on Eqs. (2.4) and (2.5). If it is an endothermic reaction, $A' > 0$, CO vol% will decline as temperature rises; if it is an exothermic reaction, $A' < 0$, CO vol% will increase with rising temperature.

2.1.1 Thermodynamics of Reduction

The thermodynamics of carbothermic reduction for iron oxides and nickel oxides have been systematically studied [1, 2]. Table 2.1 shows the reduction reactions of nickel and iron oxides by CO and corresponding binomial $\Delta_r G_m^{\ominus}$ - T for determining standard Gibbs free energy changes of the reactions at given temperatures.

According to binomial $\Delta_r G_m^{\ominus}$ - T of each reaction in Table 2.1, one can get the correlation between equilibrium gas composition and temperature for the reduction reactions of nickel oxide and ferric oxide, as shown in Fig. 2.1. NiO and Fe_2O_3 can be reduced by CO with a low concentration of CO at low reduction temperatures.

Table 2.1 $\Delta_r G_m^\ominus$ -T equations for the carbothermic reduction of nickel and iron oxides

No.	Reaction	$\Delta_r G_m^\ominus$ -T (J/mol)
(1)	$\text{NiO} + \text{CO(g)} = \text{Ni} + \text{CO}_2\text{(g)}$	$-48,298 + 1.67 T$
(2)	$1/2\text{C} + 1/2\text{CO}_2\text{(g)} = \text{CO(g)}$	$85,350 - 87.25 T$
(3)	$\text{Fe}_3\text{O}_4 + \text{CO(g)} = 3\text{FeO} + \text{CO}_2\text{(g)}$	$35,380 - 40.16 T$
(4)	$\text{FeO} + \text{CO(g)} = \text{Fe} + \text{CO}_2\text{(g)}$	$-22,800 + 24.26 T$
(5)	$3\text{Fe}_2\text{O}_3 + \text{CO(g)} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2\text{(g)}$	$-52,131 - 41.0 T$
(6)	$1/4\text{Fe}_3\text{O}_4 + \text{CO(g)} = 3/4\text{Fe} + \text{CO}_2\text{(g)}$	$-9832 + 8.58 T$

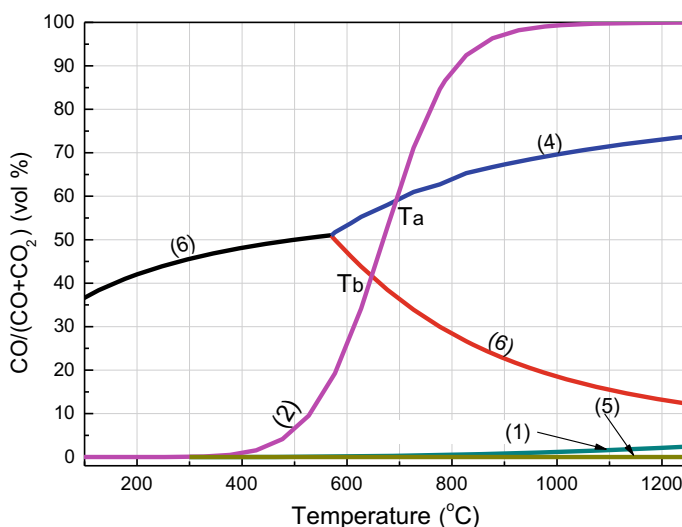


Fig. 2.1 Plot of equilibrium gas composition versus temperature for the carbothermic reduction of nickel and iron oxides

Therefore, NiO can be easily reduced to metallic nickel by CO, while Fe_2O_3 is easily reduced to Fe_3O_4 .

The gas composition equilibrium curve of the gasification reaction for solid carbon, respectively, intersects with reduction equilibrium curve of FeO and Fe_3O_4 at point T_a and T_b . If $T_a = 695^\circ\text{C}$, the concentration of CO in the corresponding equilibrium gas phase is about 59.1 vol%; if $T_b = 647^\circ\text{C}$, the concentration of CO in the equilibrium gas phase is about 40.1 vol%. Above temperature T_a , the concentration of CO in the system is higher than the equilibrium concentration of CO. Ferric oxide is finally reduced to metallic iron. Between T_a and T_b , the concentration of CO in the system is higher than the equilibrium concentration of CO in the reduction reaction of Fe_3O_4 , but lower than the equilibrium concentration of CO in the reduction reaction of FeO_x . This means that ferric oxides can transform to FeO_x . Below

temperature T_b , the concentration of CO in the system is lower than the equilibrium concentration of CO in the reduction reactions of Fe_3O_4 and FeO_x , and ferric oxide will transform into Fe_3O_4 .

Therefore, T_a and T_b divide the diagram into three zones, i.e., metallic iron stable zone with $T > T_a$, Fe_3O_4 stable zone with $T < T_b$, and FeO stable zone with $T_a > T > T_b$. As a result, when T is higher than 695°C and the concentration of CO is larger than 59.1 vol%, ferric oxide can transform to metallic iron. The selective reduction of nickel and iron oxides can be realized through controlling the atmosphere and temperature of related reduction reactions ($T < 695^\circ\text{C}$ and $\text{CO} < 59.1\text{ vol}\%$).

2.1.2 Thermodynamics of Sulfidation

The elemental sulfur is used as sulfidizing reagent for sulfidation of laterite ore. Upon flotation for sulfidized and roasted product, nickel sulfide realizes beneficiation from the raw ore. The sulfidation degree of nickel mainly depends on addition of elemental sulfur and reaction temperature [3]. Obviously, increasing reaction temperature will greatly improve thermodynamic driving force of reaction (8) to promote selective sulfidation of nickel. Table 2.2 shows the sulfidation reactions and corresponding $\Delta_r G_m^\ominus$ - T equations.

When the sulfidizing reagent is alkali/alkali-earth metal sulfate (e.g., CaSO_4 and Na_2SO_4), calcium sulfate and sodium sulfate may be firstly transformed to CaS and Na_2S during reductive roasting, which is different from sulfidation mechanism of S_2 .

The sulfidizing reagent CaSO_4 will be reduced by CO to generate CaO , CaSO_3 and CaS , etc. Table 2.3 shows corresponding chemical equations and their $\Delta_r G_m^\ominus$ - T .

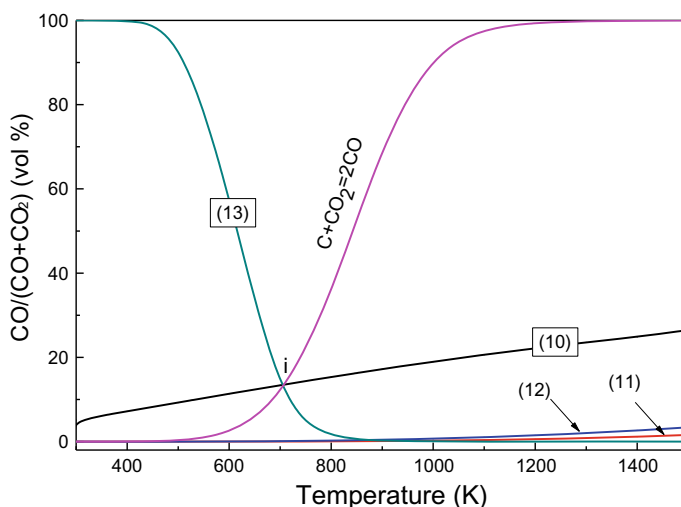
By assuming that all of above reactions are in the constant pressure system and the gas only contains CO, CO_2 and SO_2 , when the partial pressure of SO_2 is 10 vol% and the reaction reaches equilibrium, a correlation can be obtained between the equilibrium gas composition and temperature of the above reactions based on $\Delta_r G_m^\ominus = -RT \ln K^\ominus$ (Fig. 2.2). The equilibrium concentration curves of CO for reactions (13) and (10) intersect with the Boudouard reaction at point i (700 K) when the concentration of CO is 10 vol%.

Table 2.2 $\Delta_r G_m^\ominus$ - T equations of sulfidation of nickel and iron oxides by elemental sulfur

No.	Reaction	$\Delta_r G_m^\ominus$ - T (J/mol)
(7)	$4/3 \text{ NiO} + \text{S}_2 = 4/3 \text{ NiS} + 2/3 \text{ SO}_2$	$-109,958.3 + 33.9 T$
(8)	$12\text{Fe}_2\text{O}_3 + \text{S}_2 = 8\text{Fe}_3\text{O}_4 + 2\text{SO}_2$	$132,337.8 - 437.7 T$
(9)	$4/7 \text{ Fe}_2\text{O}_3 + \text{S}_2 = 8/7 \text{ FeS} + 6/7 \text{ SO}_2$	$-28,233.6 - 16.7 T$

Table 2.3 Reaction equations of $\text{Ca}_2\text{SO}_4\text{--SiO}_2$ system and their $\Delta_r G_m^\ominus\text{--}T$

No.	Reaction	$\Delta_r G_m^\ominus\text{--}T$ (J/mol)
(10)	$\text{CaSO}_4 + \text{CO(g)} = \text{CaSO}_3 + \text{CO}_2\text{(g)}$	$-2009.07 - 0.79 T$
(11)	$1/3 \text{CaSO}_3 + \text{CO(g)} = 1/3\text{CaS} + \text{CO}_2\text{(g)}$	$-13,147.46 + 0.49 T$
(12)	$1/4\text{CaSO}_4 + \text{CO(g)} = 1/4\text{CaS} + \text{CO}_2\text{(g)}$	$-10,435.98 + 0.17 T$
(13)	$\text{CaSO}_4 + \text{SiO}_2 + \text{CO(g)} = \text{CaSiO}_3 + \text{SO}_2\text{(g)} + \text{CO}_2\text{(g)}$	$18,605.73 - 42.78 T$

**Fig. 2.2** Phase equilibrium diagram of the $\text{CaSO}_4\text{--SiO}_2$ system

According to Fig. 2.2, reactions (11) and (12) will occur at low temperatures and concentrations of CO, so that CaSO_4 and CaSO_3 are easily reduced to CaS under reducing atmosphere. When the reaction temperature is higher than 700 K and the concentration of CO is larger than 10 vol%, reactions (10) and (13) may occur and the reaction system may also contain SO_2 , CaO and CaSO_3 .

To understand influence of partial pressure of SO_2 on the reactions, the calculated correlation between concentration of equilibrium gas phase and temperature under different partial pressure of SO_2 is shown in Fig. 2.3. In the temperature range 650–850 K corresponding to $P_{\text{SO}_2} = 2.5$, as P_{SO_2} increases, the equilibrium curves of gas phase for the reactions move to left bottom. When the reactions reach equilibrium, the required temperature and concentration of CO will decline slightly compared with those at $P_{\text{SO}_2} = 2.5$. Therefore, the partial pressure of SO_2 has a weak effect on the concentration of CO and temperature at the equilibrium state.

In reducing atmosphere, the reduction product of CaSO_4 (CaS) will have reaction with FeO, NiO and SiO_2 in laterite ore. Table 2.4 shows the possible reactions.

According to thermodynamic calculations, one can get the correlation between $\Delta_r G_m^\ominus$ and T of the above reactions. As shown in Fig. 2.4, if SiO_2 exists, FeO and

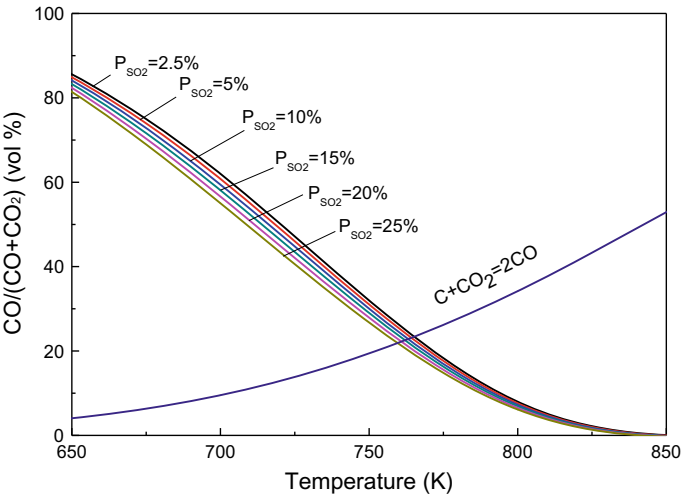


Fig. 2.3 Phase equilibrium diagram of reaction (13) under different partial pressure of SO₂

Table 2.4 Reaction equations of the CaS–FeO–NiO–SiO₂ system and $\Delta_r G_m^\ominus$ -T relationship

No.	Reaction	$\Delta_r G_m^\ominus$ -T (J/mol)
(14)	$\text{CaS} + \text{FeO} + \text{SiO}_2 = \text{CaSiO}_3 + \text{FeS}$	$-18,766.46 + 0.02 \text{ T}$
(15)	$\text{CaS} + \text{NiO} + \text{SiO}_2 = \text{CaSiO}_3 + \text{NiS}$	$-22,906.54 - 2.36 \text{ T}$
(16)	$\text{CaS} + \text{FeO} = \text{CaO} + \text{FeS}$	$2769.38 + 0.19 \text{ T}$

NiO will, respectively, react with CaS to generate FeS or NiS; if there is no SiO, CaS will not react with FeO to generate FeS. To sum up, when nickel, ferric and silicon oxides are added with calcium sulfate for reductive roasting within the temperature range 700–1600 K, possible phases in the final product mainly include Fe, Ni, FeO, FeS, NiS and CaSiO₃.

As sulfidizing reagent, sodium sulfate can be transformed to Na₂O, Na₂SO₃ and Na₂S by CO under reducing atmosphere. If SiO₂ exists in the system, the roasting product of sodium sulfate will be sodium silicate [4]. Table 2.5 shows possible chemical reactions and corresponding $\Delta_r G_m^\ominus$ -T correlations.

According to the $\Delta_r G_m^\ominus$ -T correlation of each reaction, as shown in Table 2.5, one can get the correlation between the equilibrium gas composition and temperature and the equilibrium concentration of CO in reactions (17)–(22) can be plotted, as shown in Fig. 2.5.

The $\Delta_r G_m^\ominus$ value of reaction (17) is larger than 0 within the calculated temperature range, so that Na₂SO₄ will not be transformed to Na₂SO₃ by CO. The equilibrium composition curves of gas phase for reactions (18) and (19) are located below

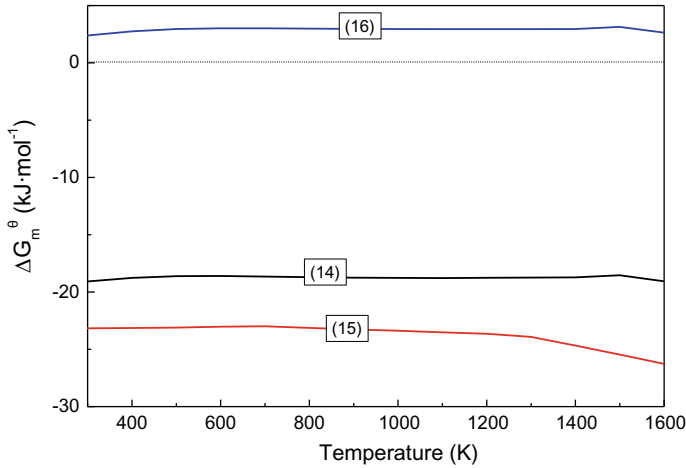


Fig. 2.4 $\Delta_r G_m^\ominus$ -T correlation of reactions for the CaS-FeO-NiO-SiO₂ system under reducing atmosphere

Table 2.5 $\Delta_r G_m^\ominus$ -T correlation of reactions for Na₂SO₄ reduction system

No.	Reactions	$\Delta_r G_m^\ominus$ -T (J/mol)
(17)	$\text{Na}_2\text{SO}_4 + \text{CO(g)} = \text{Na}_2\text{SO}_3 + \text{CO}_2\text{(g)}$	$1115.71 + 17.75 \text{ T}$
(18)	$1/3\text{Na}_2\text{SO}_3 + \text{CO(g)} = 1/3\text{Na}_2\text{S} + \text{CO}_2\text{(g)}$	$-46,533.12 + 9.43 \text{ T}$
(19)	$1/4\text{Na}_2\text{SO}_4 + \text{CO(g)} = 1/4\text{Na}_2\text{S} + \text{CO}_2\text{(g)}$	$-36,719.98 + 15.24 \text{ T}$
(20)	$\text{Na}_2\text{SO}_4 + 1/2\text{SiO}_2 + \text{CO(g)} = 1/2\text{Na}_4\text{SiO}_4 + \text{SO}_2\text{(g)} + \text{CO}_2\text{(g)}$	$184,007.51 - 238.27 \text{ T}$
(21)	$\text{Na}_2\text{SO}_4 + \text{SiO}_2 + \text{CO(g)} = \text{Na}_2\text{SiO}_3 + \text{SO}_2\text{(g)} + \text{CO}_2\text{(g)}$	$137,182.73 - 244.77 \text{ T}$
(22)	$\text{Na}_2\text{SO}_4 + 2\text{SiO}_2 + \text{CO(g)} = \text{Na}_2\text{Si}_2\text{O}_5 + \text{SO}_2\text{(g)} + \text{CO}_2\text{(g)}$	$140,442.03 - 257.72 \text{ T}$

the curve of gasification reaction of carbon, so that Na₂SO₄ and Na₂SO₃ can be transformed to Na₂S by CO within the temperature range 25–1300 °C.

The curves of reactions (20), (21) and (22), respectively, intersect with the curve of gasification reaction of carbon at points T_c , T_d and T_e ($T = 847$ °C, 647 °C and 697 °C), and the corresponding concentrations of CO are 92%, 45% and 50% respectively. As a result, when the reaction temperature T is larger than 847 °C, Na₂SO₄ reacts with SiO₂ under atmosphere of CO to generate sodium silicate and SO₂ and the generation order of sodium silicates is Na₂SiO₃ > Na₂Si₂O₅ > Na₄SiO₄.

Based on the comparison of the above-mentioned reduction reactions of Na₂SO₄ by CO, the thermodynamic driving force of reaction (19) is maximum. It indicates that Na₂SO₄ is easily transformed to Na₂S. According to thermodynamic analysis, when reduction temperature is low (695 °C), ferric oxide is easily transformed to FeO. Table 2.6 and Fig. 2.6 show possible chemical reactions and their corresponding correlation equations of $\Delta_r G_m^\ominus$ -T when Na₂S, FeO, NiO and SiO₂ co-exist.

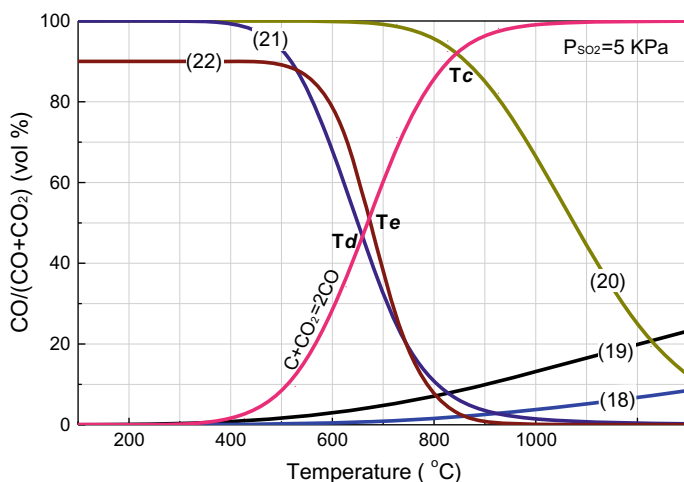


Fig. 2.5 Correlation between the composition of equilibrium gas phase of Na_2SO_4 in the carbothermic reduction and temperature

Table 2.6 Equations of sulfidation reactions for nickel and iron oxides and $\Delta_r G_m^\ominus$ -T relationship

No.	Reactions	$\Delta_r G_m^\ominus$ -T (J/mol)
(23)	$\text{Na}_2\text{S} + \text{FeO} + \text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{FeS}$	$-94,861.36 - 6.41 \text{ T}$
(24)	$\text{Na}_2\text{S} + \text{FeO} + 2\text{SiO}_2 = \text{Na}_2\text{Si}_2\text{O}_5 + \text{FeS}$	$-81,990.96 - 27.71 \text{ T}$
(25)	$2\text{Na}_2\text{S} + 2\text{FeO} + \text{SiO}_2 = \text{Na}_4\text{SiO}_4 + 2\text{FeS}$	$-112,570.32 - 111.7 \text{ T}$
(26)	$\text{Na}_2\text{S} + \text{NiO} + \text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{NiS}$	$-180,541.80 - 102.34 \text{ T}$
(27)	$\text{Na}_2\text{S} + \text{NiO} + 2\text{SiO}_2 = \text{Na}_2\text{Si}_2\text{O}_5 + \text{NiS}$	$-148,914.96 - 154.78 \text{ T}$
(28)	$2\text{Na}_2\text{S} + 2\text{NiO} + \text{SiO}_2 = \text{Na}_4\text{SiO}_4 + 2\text{NiS}$	$-123,031.99 - 81.25 \text{ T}$
(29)	$\text{Na}_2\text{S} + \text{FeO} = \text{Na}_2\text{O} + \text{FeS}$	$131,704 - 6.91 \text{ T}$
(30)	$\text{NiS} + \text{FeO} + \text{CO} = \text{FeS} + \text{Ni} + \text{CO}_2$	$-47,475 + 1.64 \text{ T}$

According to Table 2.6 and Fig. 2.6, except for reaction (29), the other reactions will easily occur within the temperature range 25–1300 °C. When SiO_2 exists, FeO and NiO will, respectively, react with Na_2S to generate FeS or NiS and Fe . The standard Gibbs free energy change of reaction (29) is larger than 0 within the temperature range 25–1300 °C, so that the reaction will not occur under this condition. When SiO_2 does not exist, Na_2S cannot react with FeO to generate FeS . The Gibbs free energy change of reaction (30) is lower than 0 within the temperature range 25–1300 °C, so that the transformation of NiS into FeS will occur easily.

According to above thermodynamic analysis, nickel oxide and ferric oxide can be transformed to their metallic states by CO , i.e., $\text{NiO} \rightarrow \text{Ni}$ and $\text{Fe}_x\text{O}_y \rightarrow \text{Fe}$, while the reduction of iron oxides follows the step-by-step reduction principle, i.e., $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. Compared with iron oxides, nickel oxides are easily

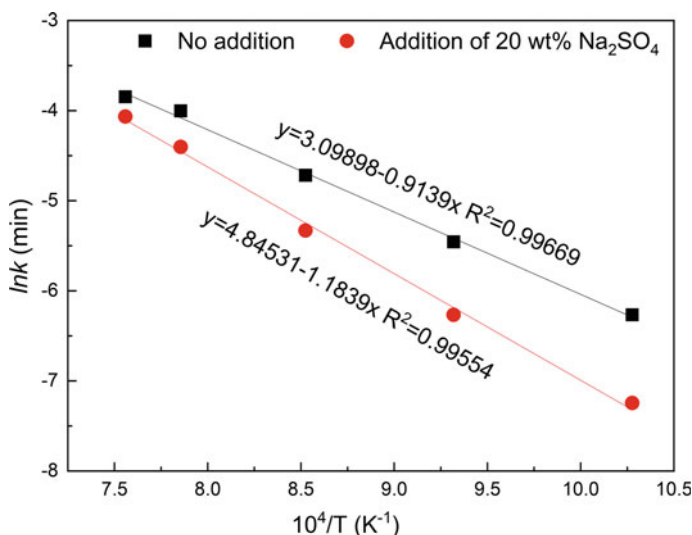


Fig. 2.6 $\Delta_r G_m^\ominus$ -T curves for sulfidation reactions of nickel and ferric oxides. Reprinted from Ref. [5], copyright 2022, with permission from Taylor & Francis

transformed into the metallic state by CO. Controlling atmosphere and temperature ($T < 695^\circ\text{C}$, $\text{CO} < 59.1 \text{ vol}\%$) will realize the selective reduction of nickel and iron oxides.

The sulfidizing reagents (elemental sulfur, calcium sulfate, sodium sulfate) have different sulfidation potential for nickel and ferric oxides. When elemental sulfur is used as sulfidizing reagent, direct sulfidation for nickel and ferric oxides can be realized and increasing reaction temperature will promote selective sulfidation of nickel. When calcium sulfate and sodium sulfate are used as sulfidizing reagents, if SiO_2 does not exist in the system, sulfidation will not occur; if SiO_2 exists, calcium sulfate and sodium sulfate react with FeO and NiO through their reaction products of CaS and Na_2S to produce FeS and NiS.

In conclusion, based on the main composition of laterite ore, the thermodynamic analysis of reduction/sulfidation of nickel and iron oxides indicates that it is feasible to control reaction temperature of system and amount of sulfidizing reagent to realize selective reduction of nickel by sulfidizing a part of iron during the process of reductive roasting.

2.2 Behaviors of Selective Reduction/Sulfidation of Laterite Ore

After mixing the sulfidizing reagent, laterite ore and water for pelletizing, the obtained green pellets were dried in a drying oven for 2 h at 110°C . 10 g of dried

pellets were put into a stainless-steel reaction tank filled with N_2 and subjected to a vertical resistance furnace (Fig. 2.7). Then, N_2 was replaced by reducing gas CO to initialize the reduction procedure when the target temperature was attained. After reduction, the reduced sample was cooled down to room temperature within the furnace with the protection of high-purity N_2 .

The chemical titration method was used to measure the contents of total iron, metallic iron, ferrous oxide, ferrous sulfide, total nickel, metallic nickel and nickel sulfide in the reduced pellets. The reduction and sulfidation degrees of products were calculated [5].

The metallization degree, reduction degree and sulfidation degree of nickel and iron in the product were used as evaluation indexes given by:

$$\gamma_{Fe} = \frac{M_{Fe}}{T_{Fe}} \times 100\% \quad (2.6)$$

$$\gamma_{FeS} = \frac{0.636FeS}{T_{Fe}} \times 100\% \quad (2.7)$$

$$R_{Ni} = \gamma_{Ni} = \frac{M_{Ni}}{T_{Ni}} \times 100\% \quad (2.8)$$

$$\gamma_{NiS} = \frac{0.647NiS}{T_{Ni}} \times 100\% \quad (2.9)$$

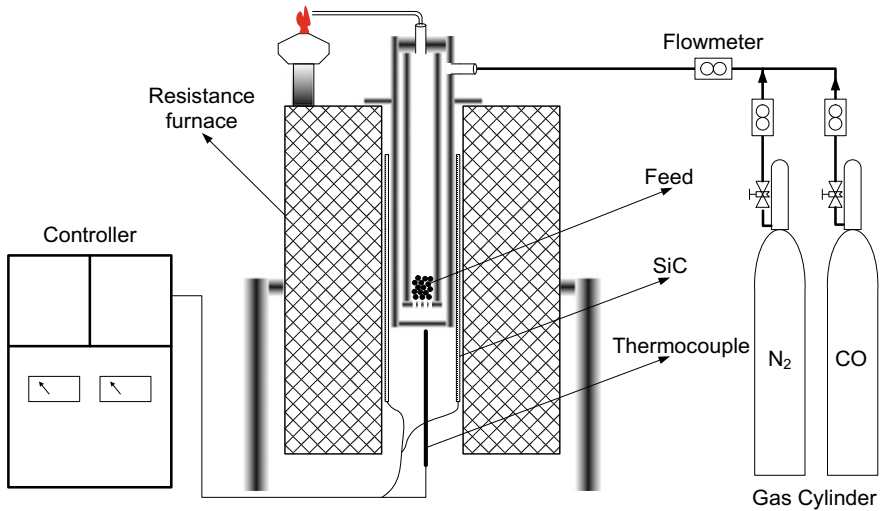


Fig. 2.7 Schematic diagram of the apparatus for reduction/sulfidation roasting of laterite ore

$$R_{Fe} = \left[1 - \frac{0.43(TFe - MFe) - 0.091FeS - 0.112FeO}{0.43TFe^0 - 0.112FeO^0} \times \frac{TFe^0}{TFe} \right] \times 100\% \quad (2.10)$$

where

- γ_{Ni} Ni metallization degree, %;
- γ_{Fe} Fe metallization degree, %;
- γ_{NiS} Ni sulfidation degree, %;
- γ_{FeS} Fe sulfidation degree, %;
- R_{Ni} Ni reduction degree, %;
- R_{Fe} Fe reduction degree, %;
- TNi total Ni content in the reduced sample, wt%;
- TFe total Fe content in the reduced sample, wt%;
- MFe content of metallic iron in the reduced sample, wt%;
- MNi content of metallic nickel in the reduced sample, wt%;
- NiS content of nickel sulfide in the reduced sample, wt%;
- MFe content of metallic iron in the reduced sample, wt%;
- FeO content of ferrous oxide in the reduced sample, wt%;
- FeS content of ferric sulfide in the reduced sample, wt%;
- TFe^0 content of total iron in the sample before reduction, wt%;
- FeO^0 content of ferrous oxide in the sample before reduction, wt%.

The interference of metallic nickel on metallic iron was excluded when the $FeCl_3$ method was used to measure metallic iron content. The calculation equation of content of metallic iron after correction is expressed as:

$$MFe = \frac{55.85 \times C \times V}{30 \times m} - \frac{2 \times 55.85}{3 \times 58.69} \times MNi \quad (2.11)$$

where

- 55.85 molar mass of iron, g/mol;
- 58.68 molar mass of nickel, g/mol;
- C concentration of potassium dichromate standard solution, mol/L;
- V volume of potassium dichromate required for titration, mL;
- m mass of the sample for titration, g.

2.2.1 Influencing Factors of Reduction/Sulfidation

2.2.1.1 Sulfidizing Reagent

When elemental sulfur (S), calcium sulfate ($CaSO_4$), sodium sulfide (Na_2S), pyrrhotite (FeS) and sodium sulfate (Na_2SO_4) were used as sulfidizing reagents,

their effects on reduction/sulfidation of nickel and iron during reductive roasting are shown in Fig. 2.8.

According to Fig. 2.8, the above sulfidizing reagents could sulfurize a portion of nickel and iron, but different sulfidizing reagents had different effects on reduction/sulfidation of laterite ore. When sulfidizing reagent was added upon the standard of 4.48% equivalent mass of sulfur, the sulfidation of nickel oxide by elemental sulfur was stronger than iron oxides and the sulfidation degree was 26.5% for nickel and

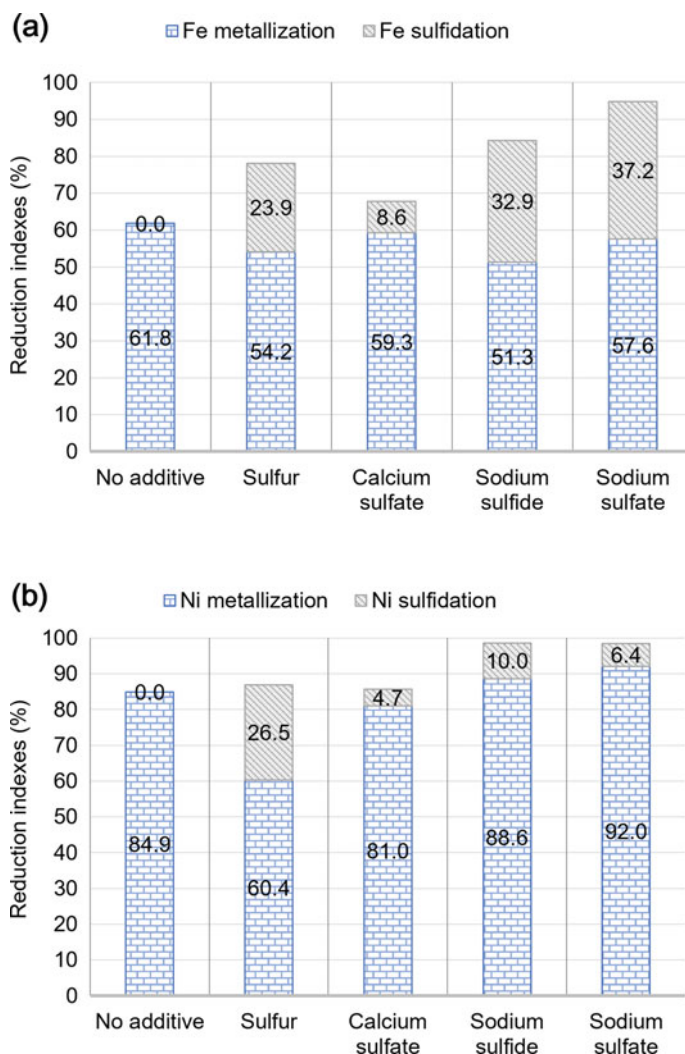


Fig. 2.8 Effects of sulfidizing reagents on reduction of iron and nickel oxides by fixing the addition of sulfidizing reagent with an equivalent mass of sulfur 4.48 wt%, reduction temperature of 1100 °C, and reduction time of 60 min

23.9% for iron. By adding calcium sulfate, the metallization degrees of nickel and iron declined compared with the case without use of the additive. The metallization degree declined from 84.9% to 81.0% for nickel and from 61.8% to 59.3% for iron. Sodium sulfide and sodium sulfate would improve the metallization degree of nickel and realize a high level of sulfidation for iron, and the sulfidation degrees of iron were 32.9% and 37.2%, respectively.

Considering its evident reduction/sulfidation effect and relatively low cost, sodium sulfate was selected as sulfidizing reagent. Figure 2.9 shows the effects of sodium sulfate on reduction and sulfidation of nickel and iron under the conditions of reduction temperature of 1050 °C, reduction time of 60 min and gas flow rate of 200 L/h (100% CO).

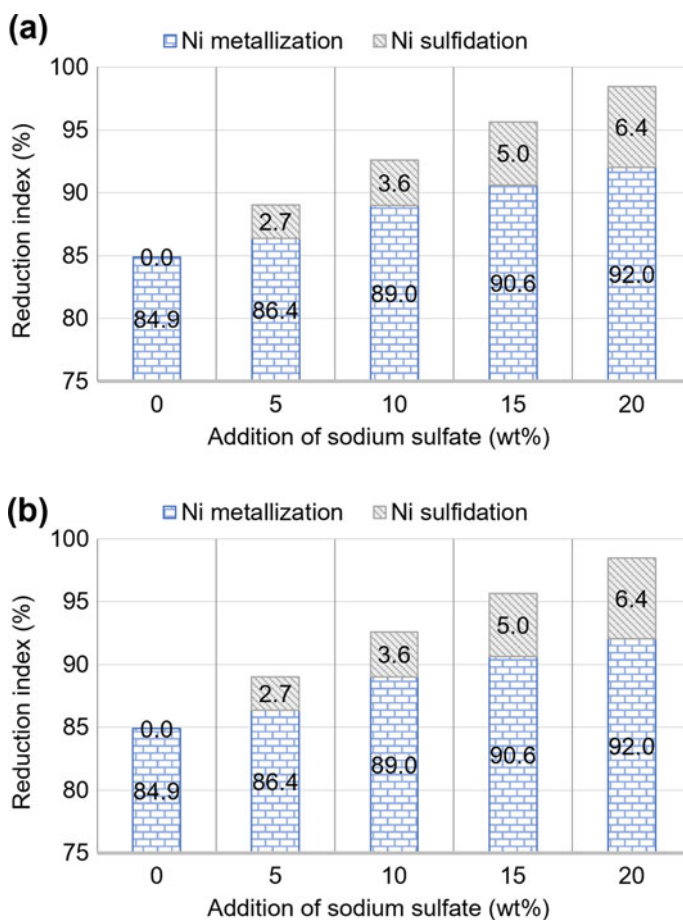


Fig. 2.9 Effects of sodium sulfate on the metallization and sulfidation degrees of nickel and iron by fixing the reduction temperature 1050 °C, reduction time 60 min, and gas flow rate of 200 L/h (100% CO): **a** Fe and **b** Ni

Table 2.7 Theoretical sulfidation degrees of Fe with different additions of sodium sulfate

Dosage of Na ₂ SO ₄ (wt%)	5	10	15	20	30	40
Theoretical sulfidation ratio of Fe (%)	8.90	17.80	26.70	35.59	53.39	71.19

As the dosage of sodium sulfate increased from 0 to 20 wt%, the metallization degree of nickel and sulfidation degrees of iron and nickel continuously improved. The metallization degree of nickel rose from 84.9 to 92.0%, while the sulfidation degree increased from 0 to 37.2% for iron and from 0 to 6.4% for nickel. However, the metallization degree of iron tended to decline from 68.4 to 57.6%. As a result, adding sodium sulfate would promote the reduction of nickel components and restrain the reduction of iron oxides.

As the addition of sodium sulfate increased, by ignoring the occupation of partial sulfur due to the sulfidation of a small amount of nickel, the theoretical sulfidation degree of Fe could be calculated. According to comparison between Fig. 2.9 and Table 2.7, when the dosage of sodium sulfate increased from 0 to 20 wt%, the sulfidation degree of iron was close to the theoretical value. As a result, in the process of reductive roasting of laterite ore with the addition of sodium sulfate, the sulfur from sodium sulfate was transformed to low-valence sulfur S²⁻ and would not emit to the atmosphere in the form of high-valence sulfur (SO₂).

2.2.1.2 Reduction Temperature

Under the conditions of gas flow rate of 200 L/h (100 vol% CO) and reduction time of 60 min, laterite ore pellets without the addition of sodium sulfate and those with the addition of 20 wt% sodium sulfate were roasted at different reduction temperatures to determine the effects of reduction temperature on metallization and sulfidation of nickel and iron.

Figures 2.10 and 2.11 show the variations of metallization degree and sulfidation degree of nickel and iron in roasted pellets at different reduction temperatures. The metallization degree and sulfidation degree of nickel and iron increased as reduction temperature increased. Increasing reduction temperature would promote reduction and sulfidation of nickel and ferric oxides.

According to Fig. 2.10, when the reduction temperature increased from 700 °C to 1050 °C, the metallization degrees of nickel and iron continuously increased without the addition of sodium sulfate. The metallization degree increased from 61.7% to 84.9% for nickel and from 13.2% to 61.8% for iron. It shows that reduction temperature strongly affected the metallization of iron.

According to Fig. 2.11, when 20 wt% sodium sulfate was added and the reduction temperature increased from 700 °C to 1050 °C, the metallization degree and sulfidation degrees of nickel and iron rose correspondingly. The metallization degree increased from 78.0% to 92.0% for nickel and from 7.0% to 57.6% for iron, while

Fig. 2.10 Effects of reduction temperature on metallization degrees of iron and nickel without the addition of sodium sulfate by fixing the flow rate of 200 L/h (100 vol% CO) and reduction time of 60 min

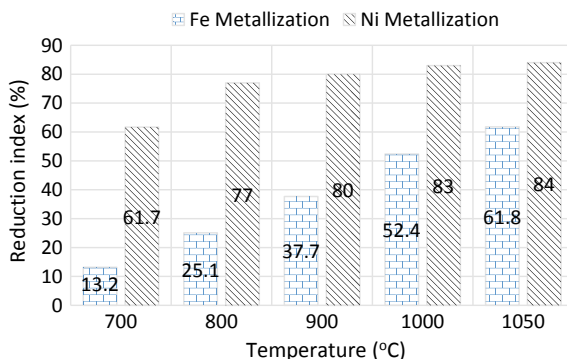
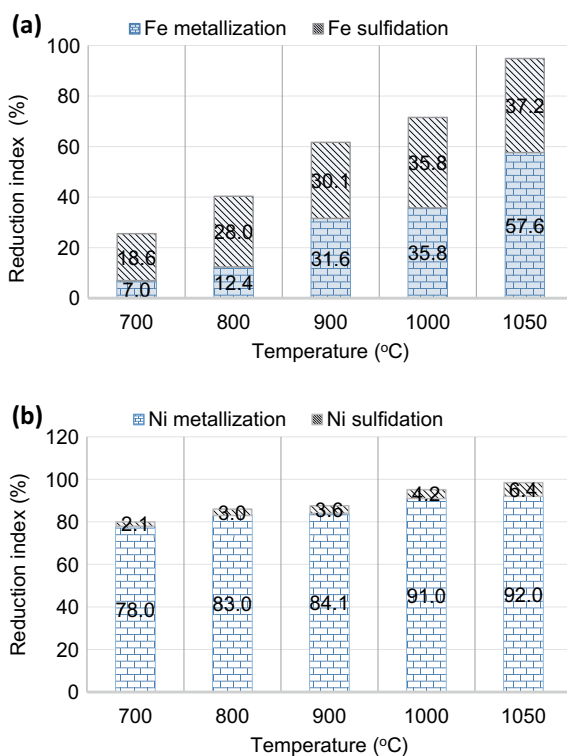


Fig. 2.11 Effects of reduction temperature on the metallization degree and sulfidation degree of (a) iron and (b) nickel with the addition of sodium sulfate by fixing the reduction time of 60 min and addition of sodium sulfate of 20 wt%



the sulfidation degree increased from 2.1% to 6.4% for nickel and from 18.6% to 37.2% for iron.

From Figs. 2.10 and 2.11, compared with the case without the addition of sodium sulfate, the metallization degree was higher for nickel and lower for iron at the same reduction temperature when 20 wt% sodium sulfate was added. The sulfidation

degree for ferric oxides was higher than that of nickel oxides. The nickel oxides were almost reduced to metallic nickel completely.

2.2.1.3 Reduction Time

Figures 2.12 and 2.13 show the effects of reduction time on the metallization degree and sulfidation degree of nickel and iron in the absence and presence of 20 wt% sodium sulfate, respectively, under the conditions of gas flow rate of 200 L/h (100% CO) and reduction temperature of 1050 °C.

As the reaction time increased, the metallization and sulfidation degrees of nickel and iron with/without the addition of sodium sulfate tended to rise. When reduction time increased to 30 min, each index changed smoothly.

According to Fig. 2.12, when sodium sulfate was not added and reduction time increased from 5 min to 60 min, the metallization degrees of nickel and iron increased continuously. The metallization degree increased from 42.0% to 84.9% for nickel and from 17.2% to 61.8% for iron.

From Fig. 2.13, when 20 wt% sodium sulfate was added and reduction time increased from 5 min to 60 min, the metallization and sulfidation degrees of nickel and iron rose continuously. The metallization degree increased from 45.3% to 92.0% for nickel and from 12.9% to 57.6% for iron, while the sulfidation degree increased from 1.2% to 6.4% for nickel and from 17.3% to 37.2% for iron. By comparison, the sulfidation degree of nickel was lower than its metallization degree.

According to Figs. 2.12 and 2.13, compared with the indexes without the addition of sodium sulfate, the metallization degree of nickel was higher and the metallization degree of iron was lower within the same reduction time when 20 wt% sodium sulfate was added. As shown in Fig. 2.14, the Ni/Fe metallization ratio in the presence of sodium sulfate was higher than that without the addition of sodium sulfate. It provided the foundation for preparing ferronickel with high nickel content.

Fig. 2.12 Effects of reduction time on the metallization degrees of iron and nickel without the addition of sodium sulfate by fixing the gas flow rate of 200 L/h (100% CO) and reduction temperature of 1050 °C

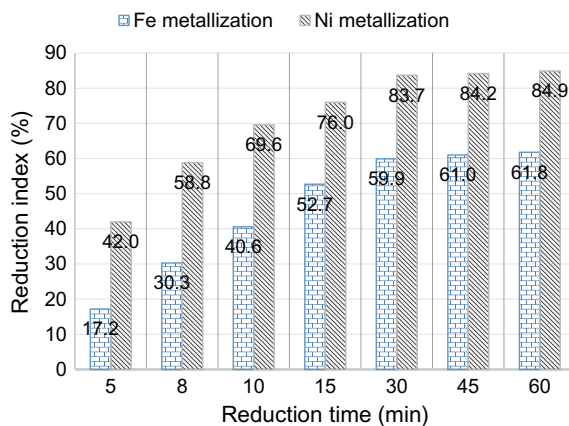
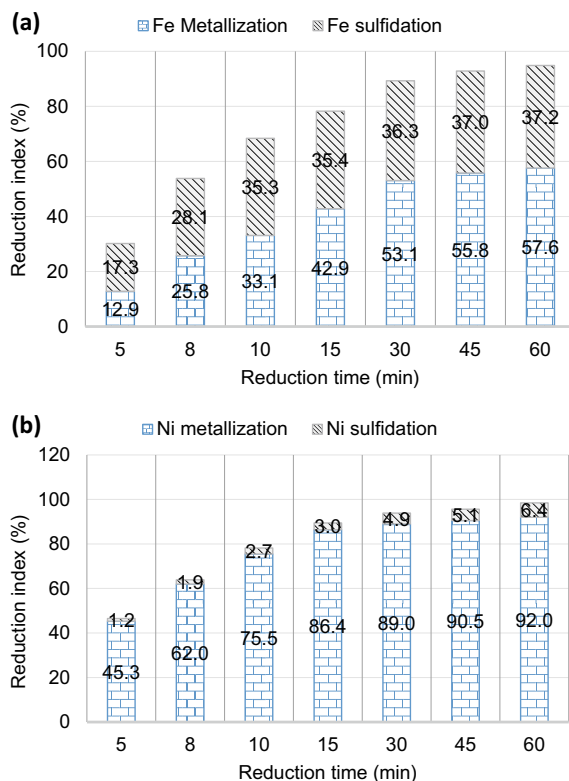


Fig. 2.13 Effects of reduction time on the metallization and sulfidation degrees of (a) iron and (b) nickel with the addition of 20 wt% sodium sulfate by fixing the gas flow rate of 200 L/h (100% CO) and reduction temperature of 1050 °C

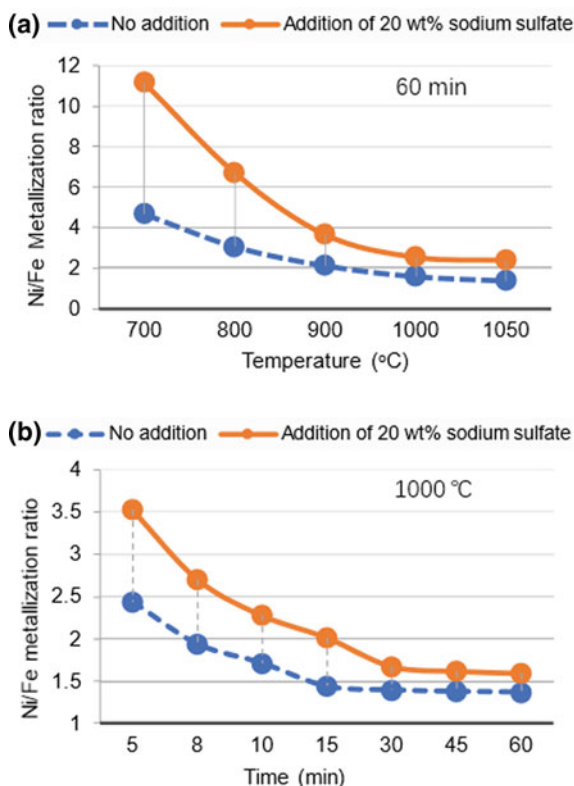


Although the sulfidation degree of iron could be increased through increasing temperature and time, the reduction process of ferric oxides was also strengthened, resulting in a constant decline of Ni/Fe metallization ratio in the reduction product. As a result, increasing temperature and time did not promote selection among reduction of ferric and nickel oxides. The optimal reduction temperature and time should be determined based on evaluation of their effects on the kinetics of reduction/sulfidation reaction and the growth of ferronickel grains simultaneously.

2.2.2 Kinetics of Reduction/Sulfidation

The methods for determining the kinetics of gas–solid reactions generally include the thermogravimetry and chemical titration methods. The thermogravimetry applies thermo-balance, spring scale or thermal gravimetric analyzer to continuously record the mass loss within the given reduction time. The chemical titration method is applied to determine the correlation between reduction rate and reduction time, based on the chemical composition before and after reduction. The thermogravimetry is

Fig. 2.14 Effects of
(a) reduction
temperature and
(b) reduction time on the
Ni/Fe metallization ratio



featured by consistent test conditions and good reproducibility and therefore is applicable to ascertain kinetics of reactions for pure ores. The chemical titration method is applicable to study reaction kinetics of complicated ores with weight loss of multiple volatile substances.

Most of current kinetics studies on reductive roasting of laterite ore apply thermogravimetry. However, the reduction and sulfidation reaction of nickel and iron oxides take place simultaneously in the roasting process, while thermogravimetry is not applicable because it cannot distinguish the reaction that results in weight loss in roasting. Therefore, the following kinetics research using chemical titration method is preferred to distinguish reduction and sulfidation effects of nickel and iron oxides in the process of reductive roasting through measuring contents of different iron and nickel phases in the reduction products.

The addition of sodium sulfate, reduction temperature and time will affect reduction and sulfidation of iron and nickel oxides in the process of reductive roasting of laterite ore. To further reveal reaction mechanism of reduction and sulfidation in the process, the isothermal reduction tests for laterite ore pellets without and with the addition of 20 wt% sodium sulfate can be used to reveal the kinetics rules with determination of rate-controlling steps of reduction and sulfidation of nickel and iron

oxides. Due to low content of nickel sulfide in the roasting products, the analysis and verification will be difficult. Therefore, the kinetics of sulfidation of nickel oxides is not discussed here.

The reduction of nickel and iron oxides in laterite ore in the presence of sodium sulfate was mainly realized through indirect reduction reaction of CO. Although the reductive roasting process involved many different types of reactions, solid–solid reactions and fluid–solid reactions were dominant. As a result, the reaction kinetics of reduction process for laterite ore could be described using the kinetic model of solid–solid reaction or fluid–solid reaction.

The rate of heterogeneous reaction could be expressed as below [7]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2.12)$$

where

- α transformation rate (reduction degree);
- t reaction time;
- T temperature;
- $k(T)$ reaction rate constant;
- $f(\alpha)$ function of kinetic model.

Table 2.8 shows the common kinetic models of solid-phase reaction. The integral form in Eq. (2.13) is usually used to calculate reaction activation energy under the isothermal condition as below:

$$g_j(\alpha) = k_j(T_i)t \quad (2.13)$$

where $g_j(\alpha) = \int_0^\alpha [f_j(\alpha)]^{-1} d\alpha$ refers to the integral form of function $f(\alpha)$ for kinetic model shown in Table 2.8.

By plotting t with $g_j(\alpha)$, the reaction rate constant can be determined. When a proper model function is available, it is able to obtain the reaction rate constants at different temperatures T_i . Then logarithmic form of the Arrhenius equation can be used to calculate the corresponding activation energy, as shown in Eq. (2.14):

$$\ln k_j(T_i)t = \ln A_j - \frac{E_j}{RT_i} \quad (2.14)$$

2.2.2.1 Kinetics of Reduction

Within the reduction temperature range 700–1050 °C, laterite ore pellets without and with the addition of 20 wt% sodium sulfate are, respectively, roasted under 100 vol% CO atmosphere with a flowrate of 200 L/h. The chemical phase analysis is conducted to measure the contents of total iron, metallic iron, ferrous oxide, ferrous sulfide, total

Table 2.8 Common kinetic models of solid-phase reaction [6]

Model	Reaction mechanism	Differential form	Integral form
		$f(\alpha)$	$g(\alpha) = kt$
$D_1(\alpha)$	One-dimensional diffusion	$\frac{1}{2}\alpha^{-1}$	$\alpha^2 = kt$
$D_2(\alpha)$	Two-dimensional diffusion	$[-\ln(1 - \alpha)]^{-1}$	$(1 - \alpha) \ln(1 - \alpha) + \alpha = kt$
$D_3(\alpha)$	Three-dimensional diffusion (JANDER equation)	$\frac{3}{2}[1 - (1 - \alpha)^{\frac{1}{3}}]^{-1}(1 - \alpha)^{\frac{2}{3}}$	$[1 - (1 - \alpha)^{\frac{1}{3}}]^2 = kt$
$D_4(\alpha)$	Three-dimensional diffusion (Ginstein-Brounshtein equation)	$\frac{3}{2}[(1 - \alpha)^{\frac{1}{3}} - 1]$	$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = kt$
$F_1(\alpha)$	First order reaction (Mampel power)	$1 - \alpha$	$-\ln(1 - \alpha) = kt$
$R_2(\alpha)$	Phase boundary control (Shrinking cylinder)	$(1 - \alpha)^{\frac{1}{2}}$	$1 - (1 - \alpha)^{\frac{1}{2}} = kt$
$R_3(\alpha)$	Phase boundary control (Shrinking sphere)	$(1 - \alpha)^{\frac{2}{3}}$	$1 - (1 - \alpha)^{\frac{1}{3}} = kt$
$A_2(\alpha)$	Two-dimensional growth of crystal nucleus (Avrami-Erofeev)	$2(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{1}{2}}$	$[- \ln(1 - \alpha)]^{\frac{1}{2}} = kt$
$A_3(\alpha)$	Three-dimensional growth of crystal nucleus (Avrami-Erofeev)	$3(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{2}{3}}$	$[- \ln(1 - \alpha)]^{\frac{1}{3}} = kt$

nickel, metallic nickel and nickel sulfide. The curves of Fe reduction degree against reduction time under different reduction temperatures based on Eq. (2.10) are shown in Fig. 2.15.

According to Fig. 2.15, as reaction proceeded, the reduction degree of iron oxides gradually increased. The reduction degree increased obviously at the early stage and tended to change slowly at the later stage until the end of reaction. When the reduction temperature rose from 700 to 1050 °C, the reduction degree increased and the reaction period for reaching equilibrium gradually shortened. For example, when sodium sulfate was not added (700 °C), it would take 45 min to reach equilibrium. As the temperature rose, the time for reaching equilibrium shortened obviously. When the temperature was 1050 °C, it took only 15 min to reach equilibrium.

The addition of sodium sulfate had significant effects on reduction of iron oxides. When 20 wt% sodium sulfate was added at the same reduction temperature, the time for reaching equilibrium for reduction of iron oxides increased and reduction degree declined. For example, it took 20 min to reach equilibrium for reduction reaction of iron oxides at 900 °C without the addition of sodium sulfate and the maximum reduction degree was about 45%. When 20 wt% sodium sulfate was added, the time

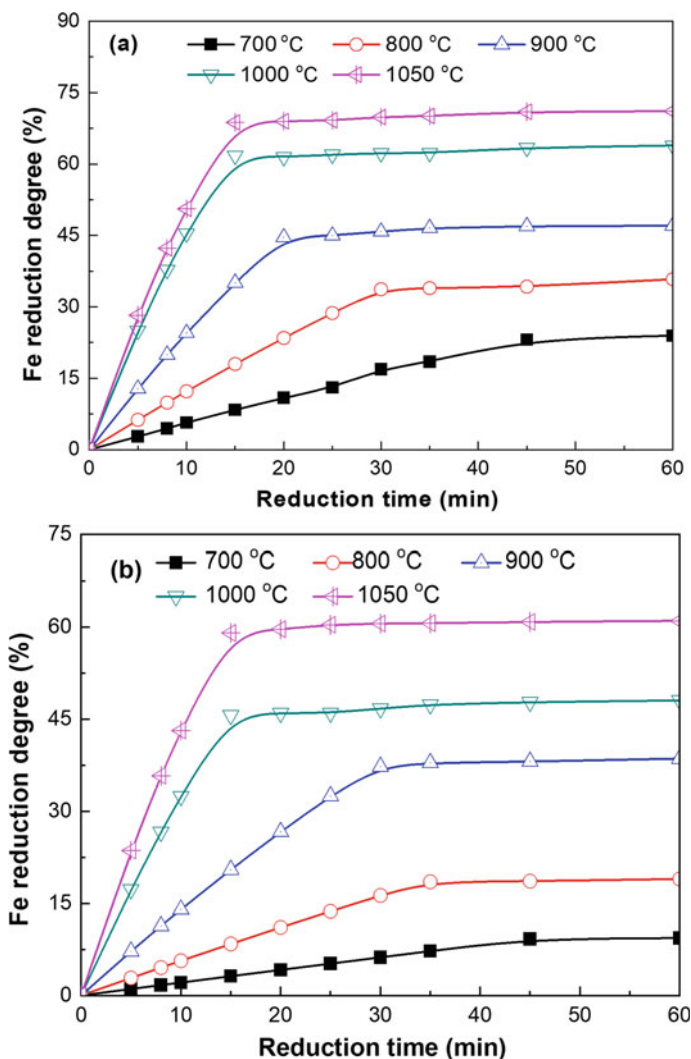


Fig. 2.15 Correlation between Fe reduction degree and reduction time at different reduction temperatures: **a** no sodium sulfate and **b** addition of 20 wt% sodium sulfate

for reaching equilibrium of reduction reaction of iron oxides increased to 30 min and the maximum reduction degree also declined to about 37%.

To determine the rate-controlling step of reduction reaction of iron oxides in laterite ore, a few kinetic function models, as shown in Table 2.8, could be used to analyze the results of isothermal reduction test for iron oxides. The reduction degree obtained by reduction for different time $g(\alpha)$ was plotted against reaction time t . The linear fitting method was used to select proper kinetic model.

When the reduction time was less than 15 min within the temperature range of test, the linear correlation between $R_3(\alpha)1 - (1 - \alpha)^{1/3}$ and reaction time t was the best, indicating that the reaction rate of iron oxides was controlled by the interface chemical reaction.

Therefore, as shown in Fig. 2.16, the reaction rate constant k value at different temperatures could be calculated. From reaction rate constants at different temperatures, the Arrhenius equation was used to calculate apparent activation energy of reduction reaction of iron oxides, i.e.:

$$k = k_0 e^{-\frac{E}{RT}} \quad (2.15)$$

According to the logarithm calculation on both sides, one can get:

$$\ln k = \ln k_0 - \frac{E}{RT} \quad (2.16)$$

where

- E activation energy, kJ/mol;
- k_0 coefficient, min^{-1} ;
- k reaction rate constant, min^{-1} ;
- R gas constant, 8.314×10^{-3} kJ/(mol·K);
- T temperature, K.

Within the temperature range 700–1050 °C, the curve of temperature $1/T$ upon $\ln k$ was plotted, being linear correlation. As shown in Fig. 2.17, the slope of straight line was $-E/R$, upon which the apparent activation reduction of energy of reduction reaction of iron oxides was calculated.

According to Table 2.9, under different conditions, the reduction degree of iron oxides increased as temperature increased and the apparent reaction rate increased obviously when the reaction temperature increased. It complied with reaction mechanism that the reduction process of iron oxides by CO was controlled by chemical reaction. When 20 wt% sodium sulfate was added, the reduction rate constant of ferric oxides at different temperatures declined. In other words, the addition of sodium sulfate restrained the reduction of iron oxides in laterite ore.

The apparent activation energy of iron oxides was 75.98 kJ/mol without the addition of sodium sulfate and was 98.43 kJ/mol with the addition of 20 wt% sodium sulfate. The activation energy increased by 22.45 kJ/mol. The activation energy could be considered as an energy barrier to be conquered in the process of reaction. When apparent activation energy of reduction of iron oxides increased after adding sodium sulfate, the obstacle that should be conquered by reduction of iron oxides increased. It indicated that adding sodium sulfate did not promote reduction of iron oxides.

Figure 2.18 shows the Ni reduction degree of the pellets without and with the addition of 20 wt% sodium sulfate as the functions of reduction temperature and time.

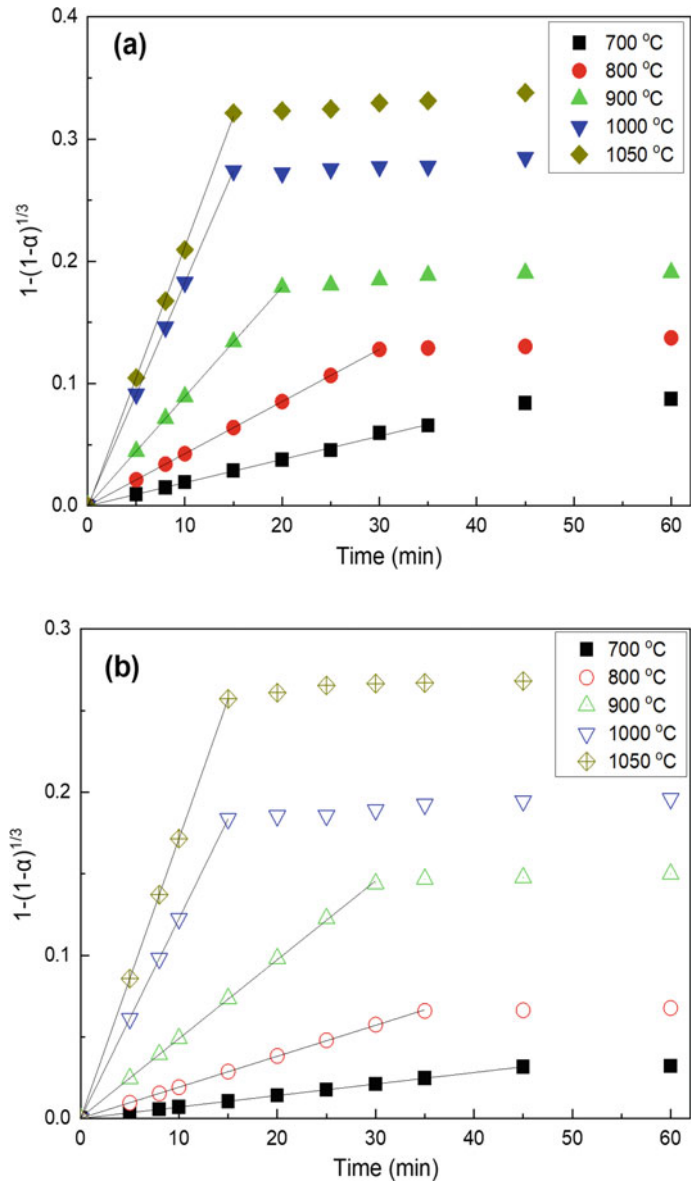


Fig. 2.16 Correlation between $R_3(\alpha)$ and t for reduction of iron oxides: **a** no sodium sulfate and **b** addition of 20 wt% sodium sulfate

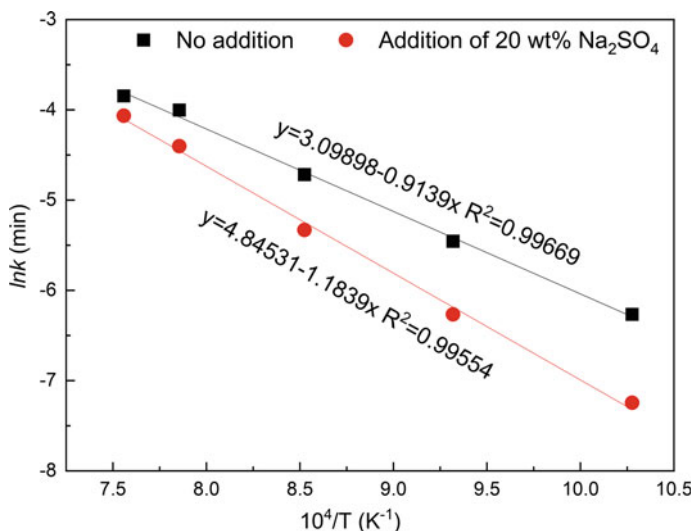


Fig. 2.17 Arrhenius correlation curve between the reaction rate constant of reduction of iron oxides and temperature

According to Fig. 2.18, as reduction time increased, reduction degree of nickel oxides with/without the addition of sodium sulfate gradually increased. The reduction degree increased obviously at the early stage of reaction and changed slightly at later stage until the reduction reached equilibrium. When the reaction temperature rose from 700 °C to 1050 °C, the reduction of nickel oxide reached equilibrium and then the reduction degree increased. However, the time for reaching equilibrium for reduction shortened gradually.

When 20 wt% sodium sulfate was added, as reduction temperature rose, the time required for reaching equilibrium for reduction of nickel oxides in laterite ore declined. It would take 30 min for nickel oxide to reach the maximum reduction degree at 700 °C, but only 15 min at 1050 °C. The increase of temperature would promote reduction of nickel oxide. In addition, compared with the condition without the addition of sodium sulfate, under the same roasting conditions, the reduction degree of nickel oxide increased when sodium sulfate was added and the time for reaching equilibrium for reaction at same reduction temperature shortened.

To determine the rate-controlling step of reduction reaction of nickel oxide in laterite ore, the kinetic function models could be applied to analyze results of isothermal reduction tests for iron oxides. The reduction degree at different reduction time in $g(\alpha)$ was plotted against reaction time t . The linear fitting method was used to select proper kinetic model. When the reduction time was lower than 15 min within the test temperature range, there was the best linear correlation between $F_1(\alpha) - \ln(1 - \alpha)$ and reaction time t . The reduction of nickel oxide in laterite ore with/without the addition of sodium sulfate was controlled by first-order chemical reaction.

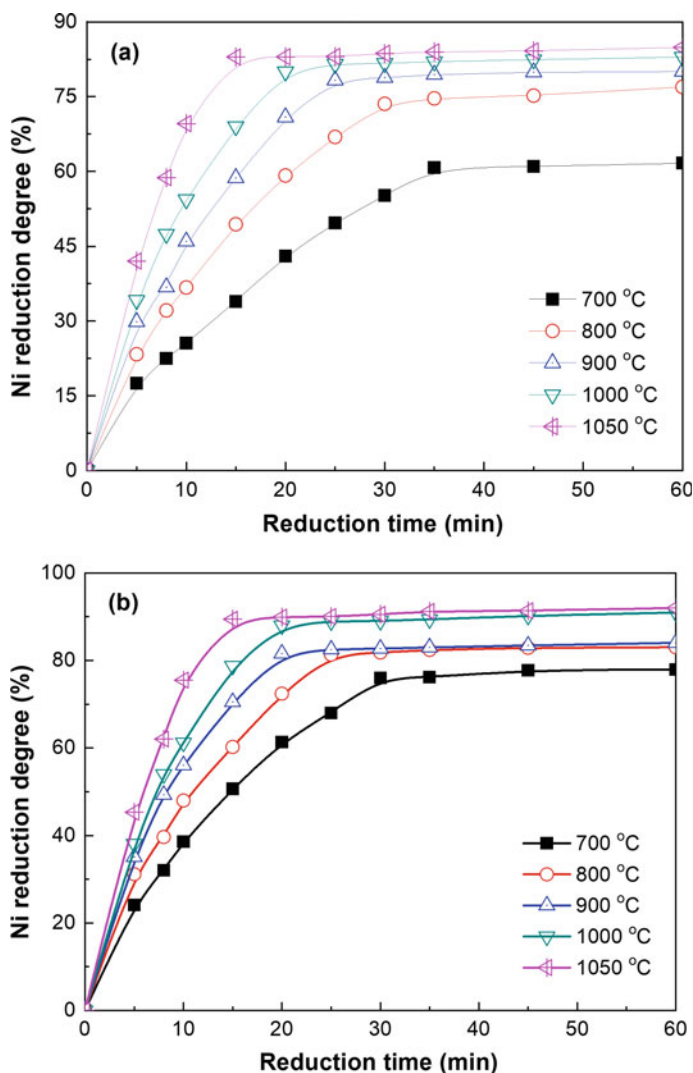


Fig. 2.18 Correlation between the reduction degree of nickel with reduction temperature and time: **a** no sodium sulfate and **b** addition of 20 wt% sodium sulfate

According to slope of each straight line shown in Fig. 2.19, the value of reaction rate constant k at different temperatures could be calculated. As shown in Table 2.10, within the temperature range 700–1050 °C, a linear correlation between temperature $1/T$ and $\ln k$ was obtained. The slope of straight line was $-E/R$, upon which the apparent activation energy of reduction of reduction reaction of nickel oxides was calculated (Fig. 2.20).

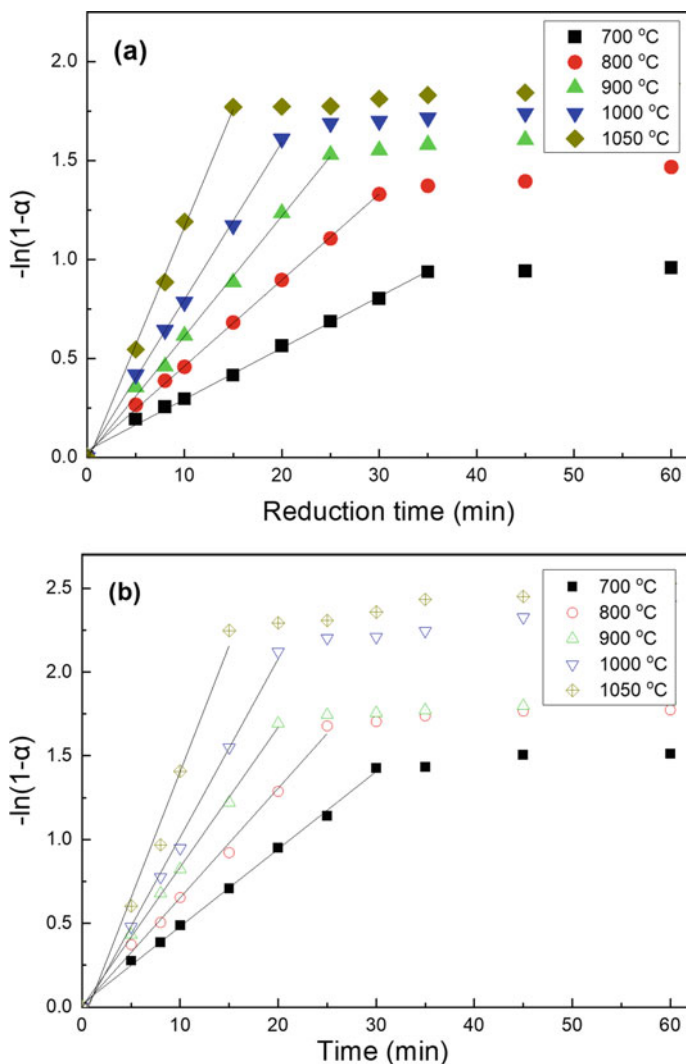


Fig. 2.19 Correlation between $F_1(\alpha)$ and t for reduction of nickel oxide: **a** no sodium sulfate and **b** addition of 20 wt% sodium sulfate

According to Table 2.10, under different conditions, the reduction rate of nickel oxides increased with temperature and the apparent reaction rate increased when the reaction temperature increased, which complied with the reaction mechanism that the reduction process of nickel oxide by CO was controlled by chemical reaction. When 20 wt% sodium sulfate was added, the reduction rate of nickel oxide increased. Hence, adding sodium sulfate could promote reduction of nickel oxides in laterite ore. According to Tables 2.9 and 2.10, under the same conditions, the reduction

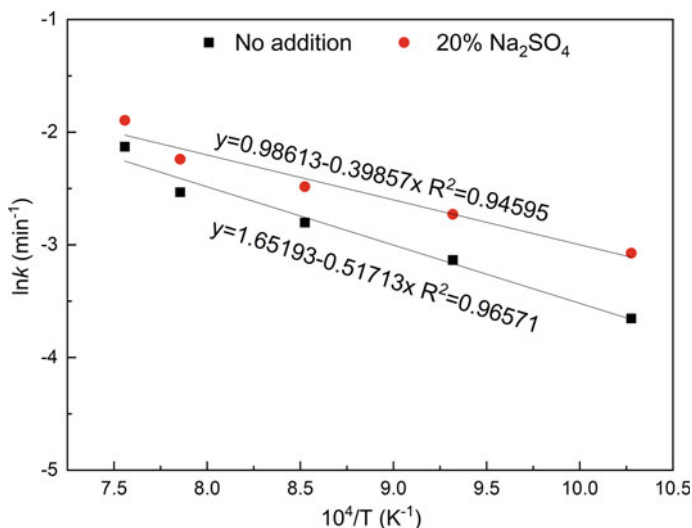


Fig. 2.20 Arrhenius correlation curve between the reduction rate constant of nickel oxide and temperature

rate of nickel oxides was higher than that of iron oxides, so that nickel oxide was more easily reduced than iron oxides. In addition, addition of sodium sulfate strongly affected the reduction rate of iron oxides.

The apparent activation energy of reduction of nickel oxide was 42.99 kJ/mol without the addition of sodium sulfate and was 33.14 kJ/mol with the addition of 20 wt% sodium sulfate. The activation energy was thus decreased by 9.85 kJ/mol. When the apparent activation energy of reduction of nickel oxides changed slightly, the obstacle that should be conquered by reduction of nickel oxide declined. It indicated that adding sodium sulfate could promote reduction of nickel oxide.

Table 2.9 Reaction rate constant of reduction of ferric oxides

Reaction rate constant $k \text{ (min}^{-1}\text{)}$	Reduction temperature ($^{\circ}\text{C}$)					Apparent activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)
	700	800	900	1000	1050	
No Na ₂ SO ₄	0.0019	0.00427	0.00894	0.01827	0.02137	75.98
20 wt% % Na ₂ SO ₄	0.00071	0.0019	0.00484	0.01225	0.01715	98.43

Table 2.10 Reduction rate constant of nickel oxides

Reaction rate constant (min^{-1})	Reduction temperature ($^{\circ}\text{C}$)					Activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)
	700	800	900	1000	1050	
No Na ₂ SO ₄	0.02591	0.04352	0.06065	0.07945	0.11901	42.99
20 wt% Na ₂ SO ₄	0.04627	0.06534	0.08344	0.10647	0.1504	33.14

2.2.2.2 Kinetics of Sulfidation

The sulfidation degree of nickel in the process of reduction was low (generally <5%) and changed slightly. Thus, the kinetics of nickel sulfidation was not further discussed. Figure 2.21 shows the correlation between Fe sulfidation degree and reaction time with the addition of 20 wt% sodium sulfate after reduction at different temperatures for variable time.

As reaction time increased, the sulfidation degree of iron gradually increased. The sulfidation degree increased obviously at early stage of reaction and tended to be stable at later stage of reaction until the end of reaction.

To determine the rate-controlling step of sulfidation reaction of iron oxides in laterite ore, the kinetic function models, as shown in Table 2.8, were used to analyze results of isothermal reduction test for iron oxides. The reduction degree at different reduction time in $g(\alpha)$ was plotted against reaction time t and then the linear fitting method was used to select proper kinetic model. When reduction time was less than 10 min within the test temperature range, the linear correlation between $F_1(\alpha) - \ln(1 - \alpha)$ and reaction time t was the best. As shown in Figure 2.22, when the reduction time was shorter than 10 min within the test temperature range, the sulfidation reaction of iron in laterite ore under action of 20 wt% sodium sulfate would be controlled by the first-order chemical reaction.

Within the temperature range 700–1050 °C, a linear correlation between temperature $1/T$ and $\ln k$ can be obtained. As shown in Fig. 2.23, the slope of straight line is $-E/R$, upon which the apparent activation energy of Fe sulfidation reaction is determined.

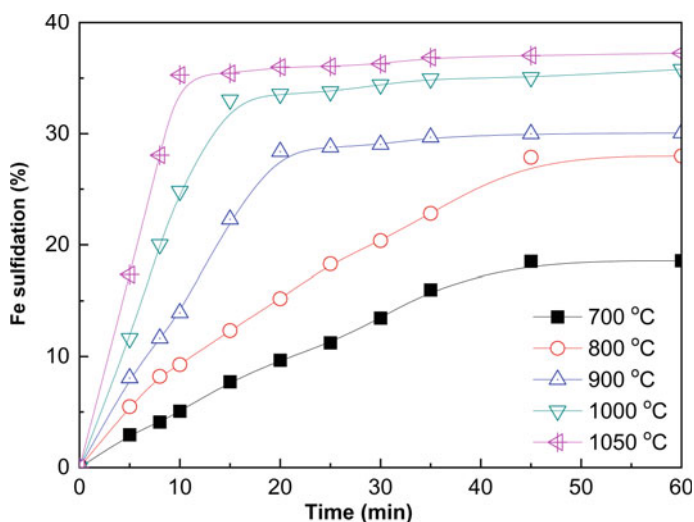


Fig. 2.21 Correlation between Fe sulfidation degree and time at different temperatures

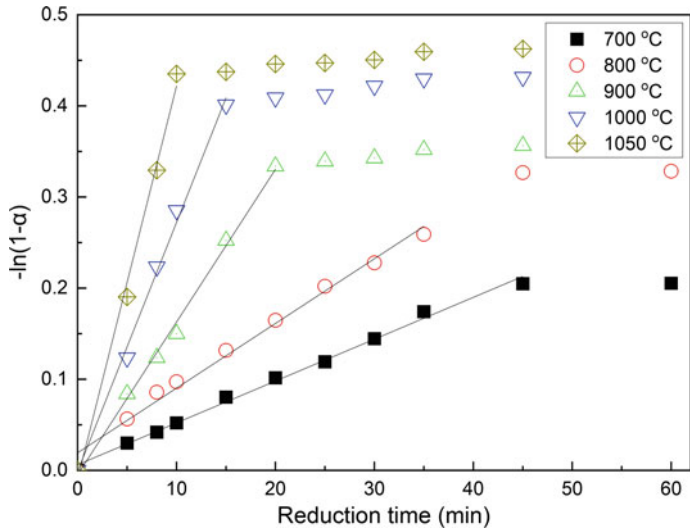
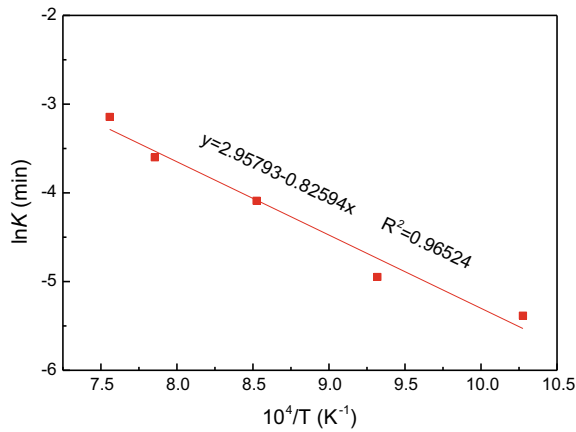


Fig. 2.22 Correlation between $F_1(\alpha)$ and t for Fe sulfidation at different temperatures in the presence of sodium sulfate

Fig. 2.23 Arrhenius correlation curve between reaction rate constant of Fe sulfidation and temperature



As shown in Table 2.11, the reduction rates of iron and nickel oxides and sulfidation rate of iron oxides increased as temperature rose. It indicated that at higher the temperature, the reactions were accelerated. At the same reduction temperature and addition of sodium sulfate, the reduction rate of iron oxides was lower than that of nickel oxides. As a result, the reduction of nickel oxides was faster than that of iron oxides. When 20 wt% sodium sulfate was added, at the same reduction temperature, the reduction rate of iron oxides declined, while the reduction rate of nickel oxides increased. As a result, the addition of sodium sulfate restrained reduction of iron oxides but accelerated reduction of nickel oxides. By comparing the reduction

Table 2.11 Reaction rate constants of sulfidation of ferric oxides at different temperatures

Temperature (°C)	700	800	900	1000	1050	Activation energy (kJ/mol)
Reaction rate constant k (min^{-1})	0.00459	0.0071	0.01676	0.02732	0.04313	69.00

rate and sulfidation rate of ferric oxides under the same conditions, the sulfidation rate of iron oxides was larger than its sulfidation rate. As a result, the sulfidation reaction of iron oxides was faster than its reduction reaction.

Table 2.12 shows the kinetics parameters and reaction mechanism of reduction and sulfidation reaction of nickel oxide. The reduction reaction of iron oxides was controlled by the interface chemical reaction, while the reduction of nickel oxide and sulfidation reaction of iron oxides were controlled by the first-order chemical reaction. The difference of activation energy also indicated different chemical reaction mechanisms. The addition of sodium sulfate had enlarged difference between the values of apparent activation energy for reduction reaction of iron and nickel oxides. Therefore, sodium sulfate would promote selective reduction between iron and nickel oxides.

In addition, the process of chemical reaction with large activation energy was easily influenced by temperature. Increasing temperature did not promote selective reduction between iron and nickel oxides. Although increasing temperature improved the sulfidation degree of iron, the metallization process of iron was not strengthened.

In conclusion, the reduction rate of iron and nickel oxides and sulfidation rate of iron oxides increased with temperature. At the same reduction temperature, the reduction rate of iron oxides is lower than that of nickel oxide, so that reduction of nickel oxide was faster than iron oxides; while sulfidation rate of iron oxides was larger than its reduction rate, so that sulfidation reaction of iron was faster than its reduction reaction. When 20 wt% sodium sulfate was added, at the same reduction temperature, the reduction rate of iron oxides declined, while the reduction rate of nickel

Table 2.12 Comparison of kinetic parameters and reaction mechanism of reduction and sulfidation reactions for iron and nickel oxides

Items	Addition of sodium sulfate (wt%)	Reduction reaction of iron oxides	Reduction reaction of nickel oxide	Sulfidation reaction of iron oxides
Apparent activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)	0	75.98	42.99	/
	20	98.43	33.14	69.00
Reaction mechanism	0	Phase boundary control $R_3(\alpha)$	First-order reaction $F_1(\alpha)$	/
	20	Phase boundary control $R_3(\alpha)$	First-order reaction $F_1(\alpha)$	First-order reaction $F_1(\alpha)$

oxide further increased. As a result, sodium sulfate has slowed down reduction of iron oxides but accelerated reduction of nickel oxide.

The addition of sodium sulfate promoted reduction of nickel oxides and prevented reduction of iron oxides, realizing selective reduction for nickel oxide and selective sulfidation of iron oxides. Besides, it could accelerate the reduction/sulfidation process and realize metallization of nickel oxide at low temperature within short time. It would guarantee high-efficiency, low-cost and selective reduction of laterite ore.

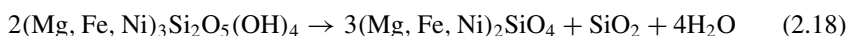
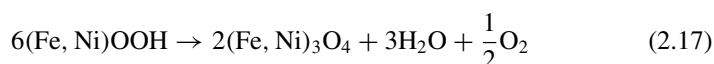
2.3 Formation and Growth of Ferronickel Particles During Solid-State Reduction

For acquiring high-quality ferronickel products, the laterite ore processing method based on solid-state reduction could be used. On the one hand, it required selective reduction for nickel and iron oxides in the process of roasting. Nickel oxide would be reduced to metallic nickel to the maximum extent and it was necessary to control the extent of reduction of iron oxides to metallic iron and thus to acquire ferronickel products with high Ni–Fe ratio. Depending on the impact of sulfidizing reagents such as sodium sulfate, the reduction of iron oxides in the process of solid-state reductive roasting of laterite ore would be prevented and the difference of nickel and iron metallization degrees increased to realize selective reduction of nickel and iron oxides in laterite ore.

On the other hand, the particle size of ferronickel in the reduction product should be sufficiently large for complete monomer separation of ferronickel using subsequent physical methods. The growth of ferronickel particles (grains) in the process of reduction was crucial for producing high-quality ferronickel by physical separation [8].

2.3.1 Phase Transformation

As shown in Fig. 2.24, as the reduction temperature increased, goethite and serpentite in laterite ore firstly had dihydroxylation (Eqs. 2.17 and 2.18) and then iron and nickel oxides were reduced to ferronickel [9]. After dehydration, lizardite would convert into hortonolite and quartz and then cinoenstatite at high temperatures (Eqs. 2.19) [10].



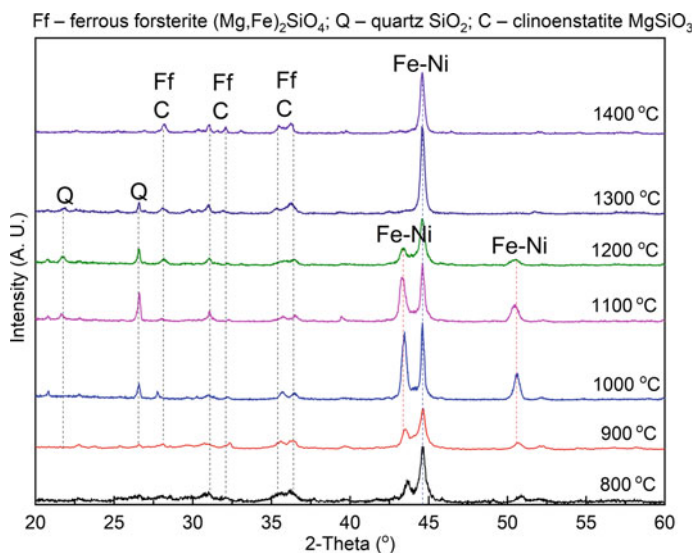


Fig. 2.24 XRD patterns of the products after reduction of laterite ore at different temperatures



According to the study of the carbothermic reduction of laterite ore by Zevgolits et al., Fe_2SiO_4 or Mg_2SiO_4 generated from reduction would wrap the oxides and prevent their further reduction.

At relative low temperatures ($<1100^\circ\text{C}$), ferronickel formed in the process of reduction existed in the form of kamacite $\alpha\text{-(Fe, Ni)}$ and taenite $\gamma\text{-(Fe, Ni)}$. When the reduction temperature rose to 1300°C , the phase of taenite disappeared and ferronickel existed in the single form of kamacite because the reduction rates of nickel and iron oxides were different. The above results indicated that the reduction rate of nickel oxide was obviously higher than that of iron oxides. As reduction temperature rose, more and more iron oxides would be reduced to metallic iron and the content of metallic iron in ferronickel constantly increased with decline of nickel content in ferronickel.

According to binary phase diagram of the Fe–Ni system (Fig. 2.25), at temperatures higher than 912°C , the taenite is stable. When the mass fraction of nickel in ferronickel is lower than 7% and temperature is lower than 912°C , taenite will transform to kamacite [11].

Figure 2.26 shows the phase compositions of the reduction products under the conditions of reduction time of 60 min and addition of 20 wt% sodium sulfate for different periods of time. Compared with phase composition without the addition of sodium sulfate, no MgSiO_3 generated in the products at different reduction temperatures when sodium sulfate was added. When reduction temperature was low ($\leq 600^\circ\text{C}$), the reduction products contained lizardite, sodium sulfate and

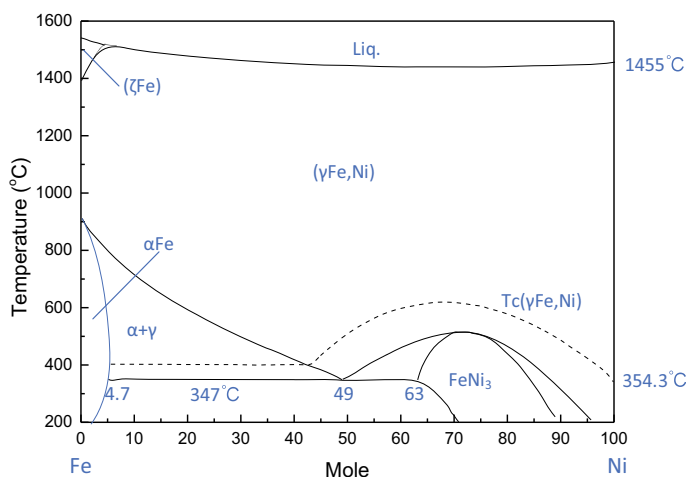


Fig. 2.25 Binary phase diagram of the Fe–Ni system

magnetite. When the reduction temperature rose to 700 °C, lizardite, sodium sulfate and magnetic iron ore in the reduction products disappeared and converted into iron sulfide (FeS), hortonolite ((Mg, Fe)₂SiO₃) and sodium silicate (Na₂SiO₃). When the reduction temperature further increased to 1100 °C, sodium silicate disappeared and transformed into sodium, magnesium and silicone ternary compound Na₂Mg₂Si₂O₇, accompanied by reduction of iron and nickel in hortonolite (Mg, Fe, Ni)₂SiO₄, while hortonolite transformed into forsterite (Mg₂SiO₄). Therefore, in the presence of sodium sulfate, the reduction of nickel oxide became easier.

The phase compositions of the reduction products from laterite ore pellets under the conditions of reduction temperature of 1100 °C and addition of 20 wt% sodium sulfate for different periods of time are shown in Fig. 2.27. When the reduction proceeded for 4 min, ferronickel and FeS formed. As a result, at reduction temperature of 1100 °C, sodium sulfate was rapidly reduced to FeS and nickel and iron oxides started to reduce. The (Mg, Fe)₂SiO₄ phase remained in the product, so that (Mg, Fe)₂SiO₄ did not transform to Mg₂SiO₄ completely. After 10 min, the (Mg, Fe)₂SiO₄ phase disappeared, and nickel and iron in (Mg, Fe)₂SiO₄ were reduced. As reaction time further increased, the intensity of FeS peak and (Mg, Fe)₂SiO₄ peak increased.

Figure 2.28 shows the effect of sodium sulfate on the phase transformation of laterite ore during reductive roasting. On the one hand, sodium sulfate had reactions with the MgO·SiO₂, 2MgO·SiO₂ and SiO₂ in the MgO–SiO₂ system to destroy structure of silicate and other gangue minerals and to release iron and nickel. On the other hand, sodium sulfate was easily reduced to Na₂S under reducing atmosphere and Na₂S would promote the formation of FeS after its reaction with SiO₂ and FeO. When the reduction temperature was higher than 700 °C, the main phases in reductive roasting system of laterite ore included Fe, Ni, FeO, FeS and sodium silicate.

L – $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$; M – Fe_3O_4 ; T – Na_2SO_4 ; Ff – Ferrous forsterite $(\text{Mg},\text{Fe})_2\text{SiO}_4$;
 F – Mg_2SiO_4 ; Tr – FeS; N – Na_2SiO_3 ; NMS – $\text{Na}_2\text{Mg}_2\text{Si}_2\text{O}_7$

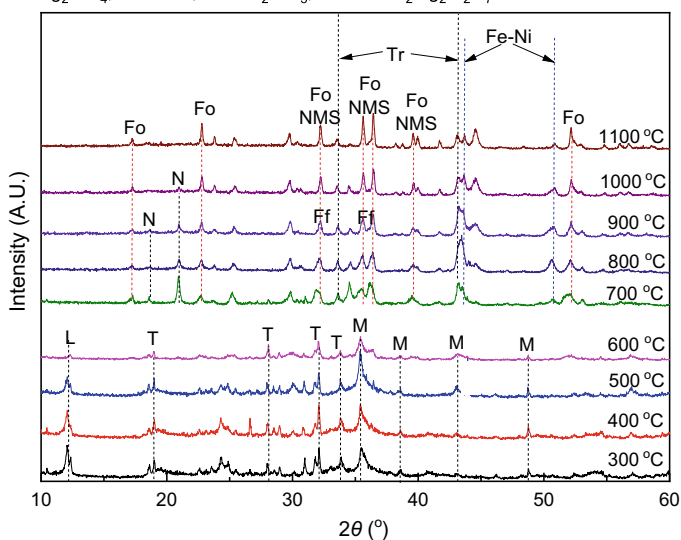


Fig. 2.26 XRD results for reduction products of laterite ore at different temperatures with addition of 20 wt% sodium sulfate (reduction time 60 min)

Liz – $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$; Mag – $(\text{Fe},\text{Ni})_3\text{O}_4$; Th – Na_2SO_4 ; NMS – $\text{Na}_2\text{Mg}_2\text{Si}_2\text{O}_7$;
 Ffo – Ferrous forsterite $(\text{Mg},\text{Fe})_2\text{SiO}_4$; Fo – Mg_2SiO_4 ; Tr – FeS; Nat – Na_2SiO_3

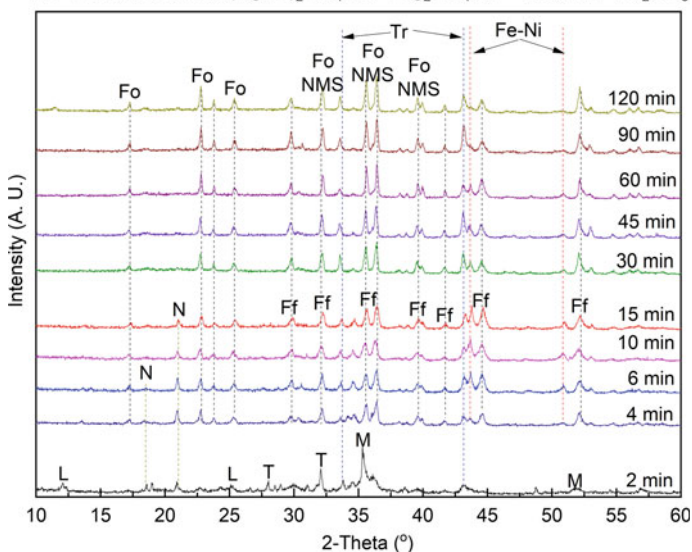


Fig. 2.27 XRD patterns of the products of laterite ore obtained by reduction for different reduction time with the addition of 20 wt% sodium sulfate (reduction temperature 1100 °C)

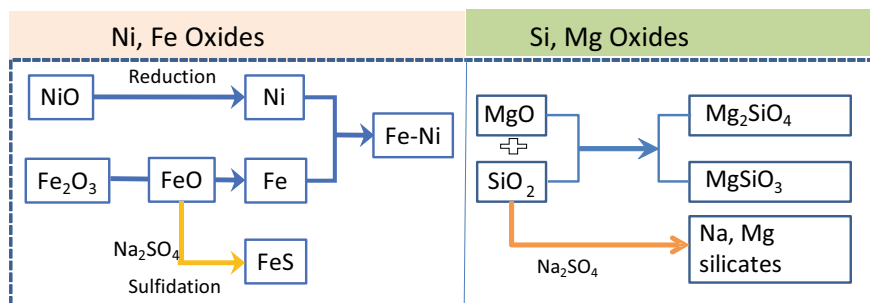


Fig. 2.28 Phase transformation of laterite ore with the addition of sodium sulfate during reductive roasting

FeS and $\text{Na}_2\text{Mg}_2\text{Si}_2\text{O}_7$ appeared in the reduction product, while enstatite MgSiO_3 disappeared.

After reduction for 4 min, ferronickel and FeS co-existed. As the reduction time increased, the number of ferronickel grains in the pellets increased obviously and ferronickel grains completely combined and grew. As a result, the generation of FeS in the process of reduction significantly promoted growth of ferronickel grains.

According to phase transformation rules of laterite ore, there were strong effects of addition of sodium sulfate. On the one hand, sodium sulfate reacted with the MgO-SiO_2 system ($\text{MgO} \cdot \text{SiO}_2$, $2\text{MgO} \cdot \text{SiO}_2$ and SiO_2) to generate sodium, magnesium and silicone ternary compound $\text{Na}_2\text{Mg}_2\text{Si}_2\text{O}_7$. On the other hand, sodium sulfate was easily reduced to Na_2S under reducing atmosphere and Na_2S would react with FeO to generate FeS. Therefore, new phases, including the sodium, magnesium and silicone ternary compound and FeS, might reduce softening temperature for reduction of laterite ore in the presence of sodium sulfate.

2.3.2 Softening-Melting Property

The laterite ore was added with different dosages of sodium sulfate and then mixed with proper volume of water. The mixture was used to make materials into standard pyrometric cones with bottom length of 5 mm and height of 12 mm. The standard pyrometric cones were put on corundum pellet and then into horizontal tube furnace with initial temperature of 900 °C for reductive roasting (CO gas flow rate of 5 cm/s and total gas flow rate of 350 L/h). The heating rate of tube furnace was 4 °C/min and the maximum roasting temperature was 1400 °C. The front camera in the tube furnace took photos every 2 s to observe changes of shape of standard pyrometric cone with temperature. Besides, the image analysis software in the system monitored shape changes of the standard pyrometric cones to measure softening temperature.

The softening and melting properties of mixed materials included: (1) deformation temperature T_D : Temperature when top point of standard pyrometric cone turned round or bended; (2) softening temperature T_S : Temperature when standard pyrometric cone deformed to approximate hemisphere; (3) flow temperature T_F : Temperature when standard pyrometric cone melted into thin layer with height below 1.5 mm. The view of experimental equipment and shape changes of corresponding pyrometric cones at the above three temperatures are shown in Fig. 2.29. Figure 2.30 shows the changes of shape corresponding to various softening temperatures. Figure 2.31 shows the photo of horizontal tube furnace [12].

The laterite ore dried and ground was, respectively, added with different amounts of Na_2SO_4 and mixed with a proper amount of water, and then was used to make materials into standard pyrometric cones with bottom length of 5 mm and height of 12 mm. Besides, the softening temperature was measured under the 100% CO atmosphere and the results are shown in Fig. 2.32.

According to Fig. 2.32, under reducing atmosphere, as the addition of sodium sulfate increased, the deformation temperature T_d , softening temperature T_s and flow temperature T_f constantly declined.

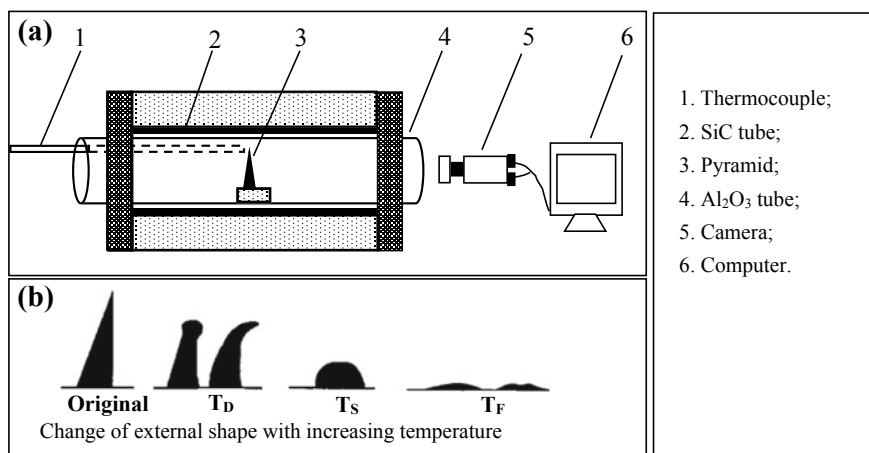


Fig. 2.29 (a) Schematic illustration of horizontal tube furnace and (b) change of sample shape with temperature

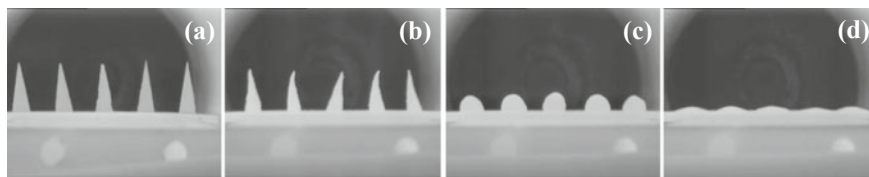
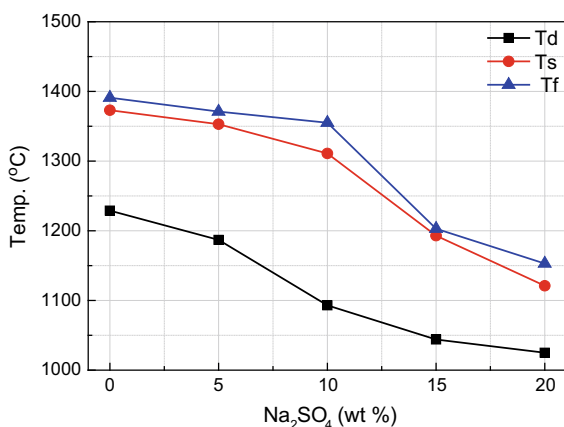


Fig. 2.30 Photos showing the softening-melting properties of the samples: **a** original shape, **b** deformation temperature, **c** softening temperature, and **d** flow temperature

Fig. 2.31 Photo of horizontal tube furnace



Fig. 2.32 Softening temperature of laterite ore mixed with different amounts of Na_2SO_4 under reducing atmosphere, reprinted from Ref. [8], copyright 2022, with permission from Taylor & Francis



The deformation temperature T_d , softening temperature T_s and flow temperature T_f of laterite ore without the addition of sodium sulfate under reducing atmosphere were 1229, 1373 and 1391 °C. The softening temperature was relatively high. When 20 wt% sodium sulfate was added, three softening temperatures of materials greatly declined, namely 1025 °C, 1121 °C and 1153 °C, respectively. The decline of softening temperature could also be partially revealed by the appearance of reduced pellets. According to Fig. 2.33, the volume of reduced pellets of laterite ore added with 20 wt% sodium sulfate decreased obviously because 1100 °C was higher than deformation temperature of the system (1025 °C). As a result, along with the formation of liquid phase, the pellets became densified.

According to above results, under 100 vol% CO reducing atmosphere, the softening temperature of laterite ore could be declined over 100 °C through adjusting the addition of sodium sulfate. Based on difference of mass transfer coefficient for solid and liquid-state materials, the generation of liquid phase could greatly accelerate mass transfer in the reductive roasting process, promoting growth and aggregation



Fig. 2.33 Appearance of reduced pellets of laterite ore (1100 °C, 60 min)

of ferronickel grains. It would be beneficial to reduction and subsequent grinding and separation.

2.3.3 Microstructure

Figure 2.34 shows microstructures of the pellets reduced for 60 min at different temperatures without the addition of sodium sulfate. According to Fig. 2.34, the structure of reduced pellets of laterite ore was dense. At low temperatures (≤ 1000 °C), the size of ferronickel grains in the reduced pellets was small and increased with temperature. When the temperature reached 1100 °C, there were obvious ferronickel grains and clear boundaries between ferronickel grains (bright white) in the reduced pellets and gangue mineral (dark grey). However, the grains did not grow completely and the range of particle size was 5–10 μm . The ferronickel grains were scattered in the matrix of forsterite and large-scale grain aggregation was not formed. However, the ferronickel grains did not realize complete monomer separation in ore grinding and therefore could not be separated from non-magnetic gangue mineral through magnetic separation.

Figure 2.35 shows the microstructure of the pellets after reductive roasting for different periods of time in the presence of 20 wt% sodium sulfate.

According to Figure 2.35, compared with the case without the addition of sodium sulfate, the pores of reduced pellets in the presence of 20 wt% sodium sulfate increased, and the number of ferronickel grains in the reduced pellets at the same reduction temperature was larger. At 800 °C, there were a large number of ferronickel grains with small size, within the range 2–8 μm . As the reduction temperature rose, the size of ferronickel grains gradually increased and their boundary with gangue mineral became clear.

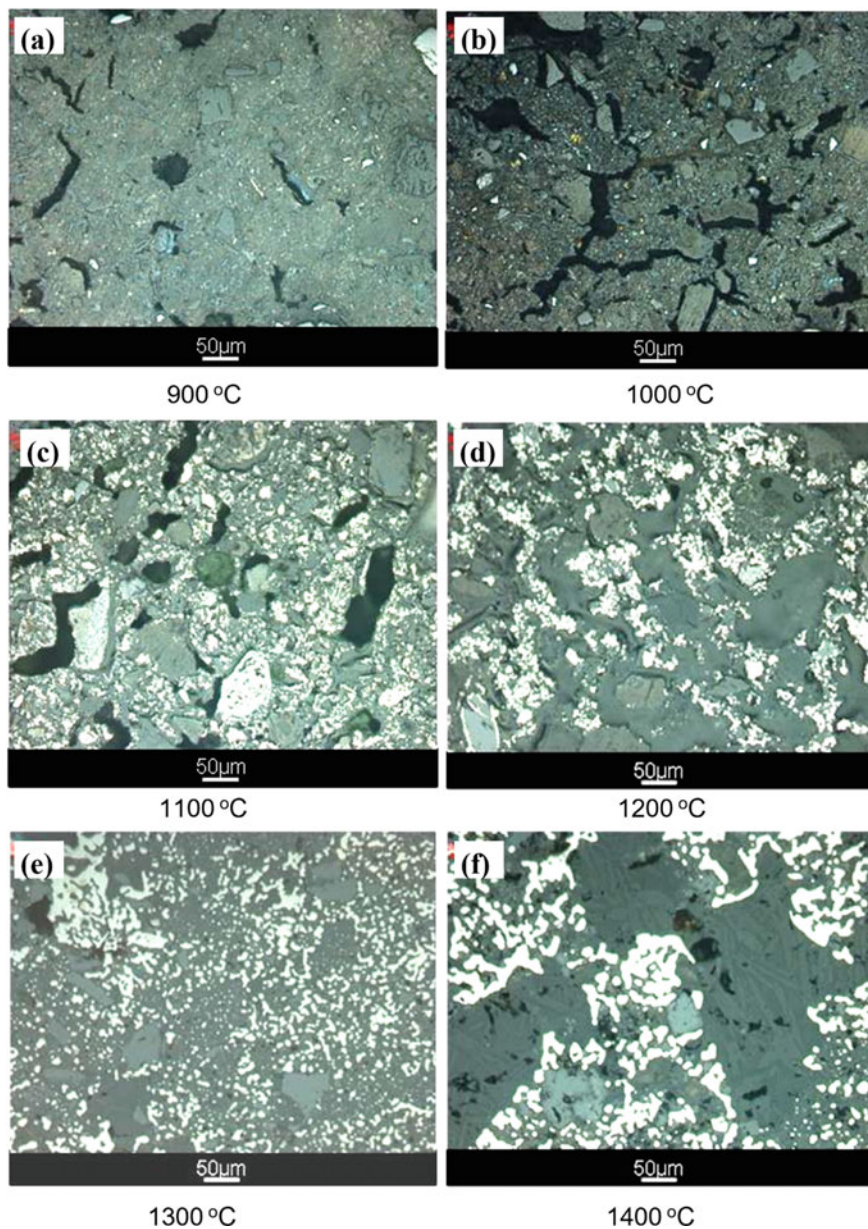


Fig. 2.34 Microstructures of the pellets after reductive roasting without the addition of sodium sulfate (bright white substances showing ferronickel metal grains)

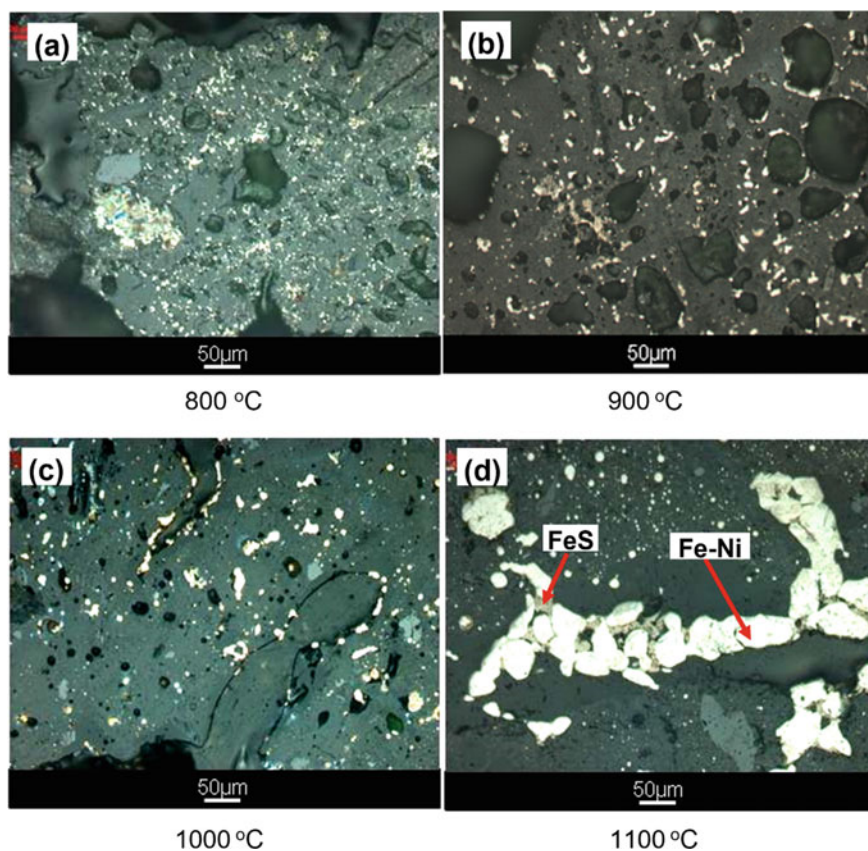


Fig. 2.35 Microstructures of the pellets after reductive roasting in the presence of 20 wt% sodium sulfate (bright white substances showing ferronickel metal grains and light yellow substances showing FeS), reprinted from Ref. [13], copyright 2022, with permission from Elsevier

When the reduction temperature reached 1100 °C, ferronickel grains precipitated, combined and grew along boundary of gangue. The boundary between ferronickel grain in the pellets and gangue was extremely clear. The ferronickel grains in the pellets grew completely. Most of internal ferronickel grains migrated to edges and combined. Besides, the boundaries between grains of FeS (light yellow), ferronickel and gangue minerals were extremely clear.

Figure 2.36 shows microstructures of the pellets reduced at 1100 °C for different time with the addition of 20 wt% sodium sulfate.

After reductive roasting for 15 min, ferronickel grains were still small. The boundary with grey gangue mineral was clear, while the size of small grains was only 1–2 μm and they closely combined with grey gangue mineral.

When reduction roasting proceeded for 30 min, the number of ferronickel grains in pellets increased obviously and these grains completely combined and grew. The

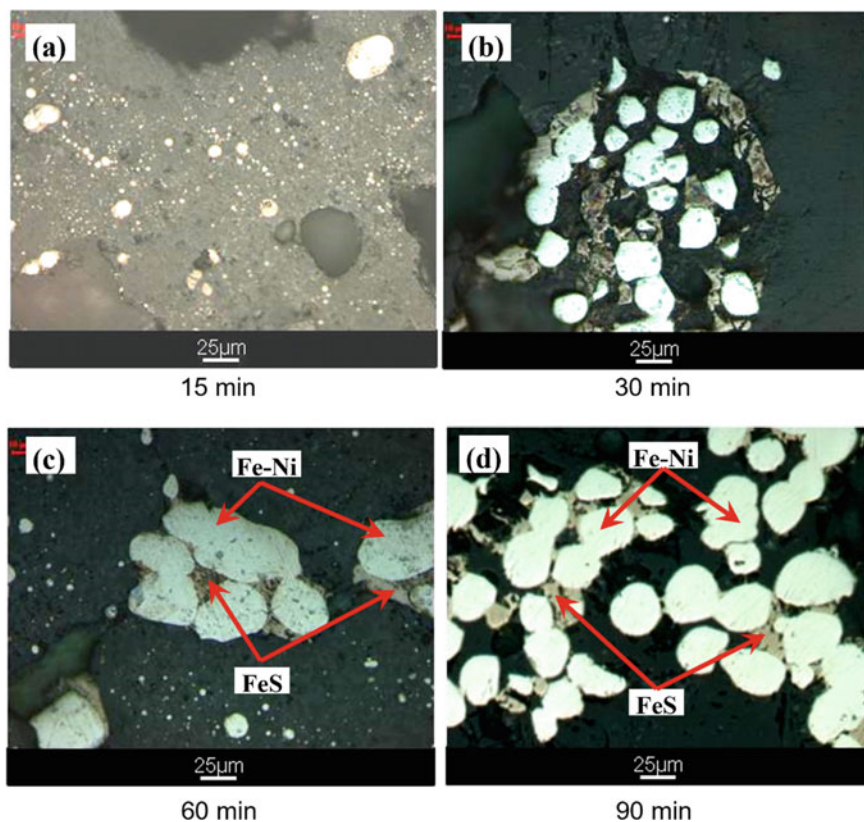


Fig. 2.36 Microstructures of pellets after reduction for different time in the presence of 20 wt% sodium sulfate (bright white substances showing ferronickel metal grains and light yellow substances showing the existence of FeS)

particle size reached about 15–30 μm and the boundary with grey gangue mineral and FeS grain was extremely clear, which would accelerate separation of metallic ferronickel grain and gangue minerals in ore grinding. Meanwhile, FeS grains had also combined and grown obviously and surrounded ferronickel grains to form rings. The range of its particle size was 15–30 μm.

When reduction roasting proceeded for 60 min, most of small grains aggregated and grew into large particles, with the size of 20–40 μm. The boundary with grey gangue mineral and FeS grain was clear. However, the number of FeS grains slightly declined and the particle size decreased. When reduction roasting proceeded for 90 min, most of small grains have grown and combined obviously into large particles and formed into droplet along grain edges, with smooth angle and uniform particle size of 50–100 μm. Besides, the boundary with grey gangue mineral and FeS grain was clear, which would accelerate separation of ferronickel grain with

gangue mineral in ore grinding. Meanwhile, FeS changed slightly and remained close connection with ferronickel grain.

According to microstructure of reduced pellets of laterite ore in the presence/absence of sodium sulfate, the structure of reduced pellets was dense. The number of ferronickel grains increased with temperature. When reduction temperature continued to rise, a portion of ferronickel grains and gangue mineral were wrapped. Compared with the condition without the addition of sodium sulfate, the pores of reduced pellets with the addition of 20 wt% sodium sulfate increased. At the same reduction temperature, there were more ferronickel grains in the reduced pellets. As reduction temperature increased, the size of ferronickel grain gradually increased, the boundary between ferronickel grain and gangue minerals was clear. In particular, the boundaries between the grains of FeS, ferronickel, and gangue minerals were also extremely clear.

The image analysis software was used to further measure size of ferronickel grain and average sizes of ferronickel grain in reductive roasting pellets under various conditions. An optical microscope (500-times DMI5000M optical microscope; German Leica) was used to observe microstructure of ore and an image analysis software (Image-Pro Plus 6.0) was used to measure area of ferronickel grain. The sectional positions of two pellets were monitored. 8 fields of vision at edge of pellets and 8 fields of vision in middle zone, total 16 fields of vision for one pellet and 32 pictures were taken under same condition for grey processing. After obtaining grey-scale map, the image analysis software was used to mark bright white ferronickel grain in the pictures with colors. The area percentage of ferronickel grains in the whole picture and number of mineral grains were determined in the target field of vision. Then, the average size area of ferronickel grains in the sample was calculated. Due to irregular shape of ferronickel grain and unbalanced distribution, it was difficult to determine shape feature of grain in pellets. In order to analyze problems conveniently, the ferronickel grains were considered to be spherical, i.e., round shape in two-dimensional plane for further calculation of particle size of single ferronickel grain. Due to different reduction effects in edge position and middle position and different volume, based on volume weight ratio, one may calculate the specific value between volume of ferronickel grains at edge position and the volume of ferronickel grains in the middle area, being 8. The ferronickel grains were sorted from small to large sizes after calculating volume of ferronickel grains in the edge and middle position. If the proportion of ferronickel grains from $D_{(\min)}$ (minimum ferronickel grain) to D_{10} in total volume was 10%, then volume proportion of ferronickel grains from $D_{\min}$ to D_{50} in total volume was 50% and it would be 90% from $D_{\min}$ to D_{90} . $D(0.5)$ denotes the average size of ferronickel grain under the above conditions (Fig. 2.37).

Figure 2.38 shows the sizes of ferronickel grains in the pellets after reduction at different temperatures with/without the addition of sodium sulfate. The size of ferronickel grain had increased obviously. After reduction for 60 min at 1100 °C for laterite ore pellets, the average size of ferronickel grains increased from 7.4 to 48.6 μm . As a result, increase of size of ferronickel grain would facilitate separation from gangue mineral in ore grinding to further improve effect of magnetic separation.

Fig. 2.37 Shooting points for measuring the particle size of ferronickel in the pellets

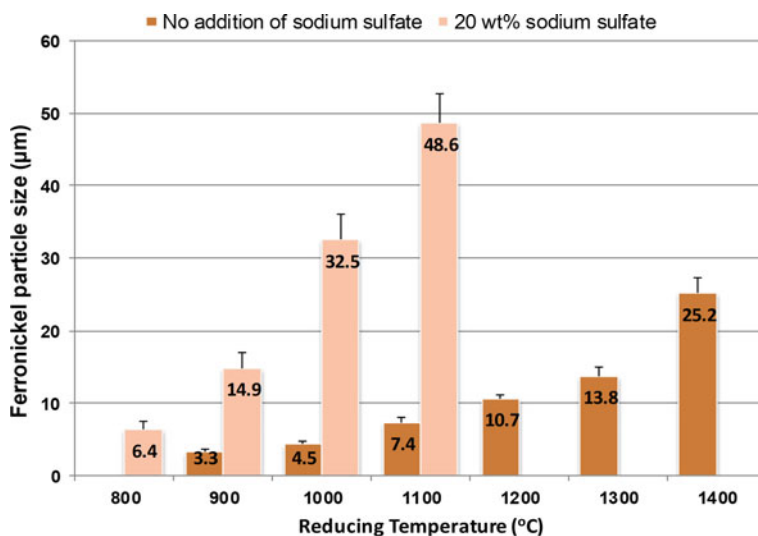
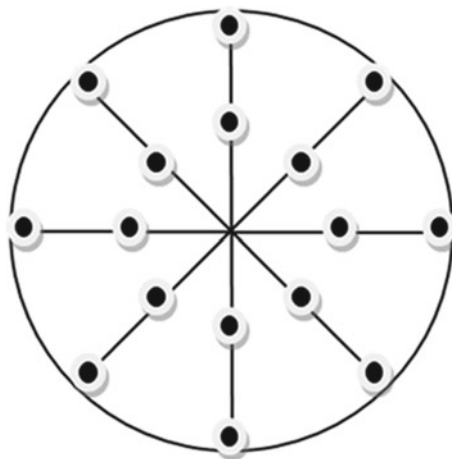


Fig. 2.38 Sizes of ferronickel grains in the reduced pellets of laterite ore at different reduction temperature

According to microstructures of reduced pellets of laterite ore added with 20 wt% sodium sulfate, the generation mechanism of liquid phase in reduction system was proposed, as shown in Figs. 2.39 and 2.40.

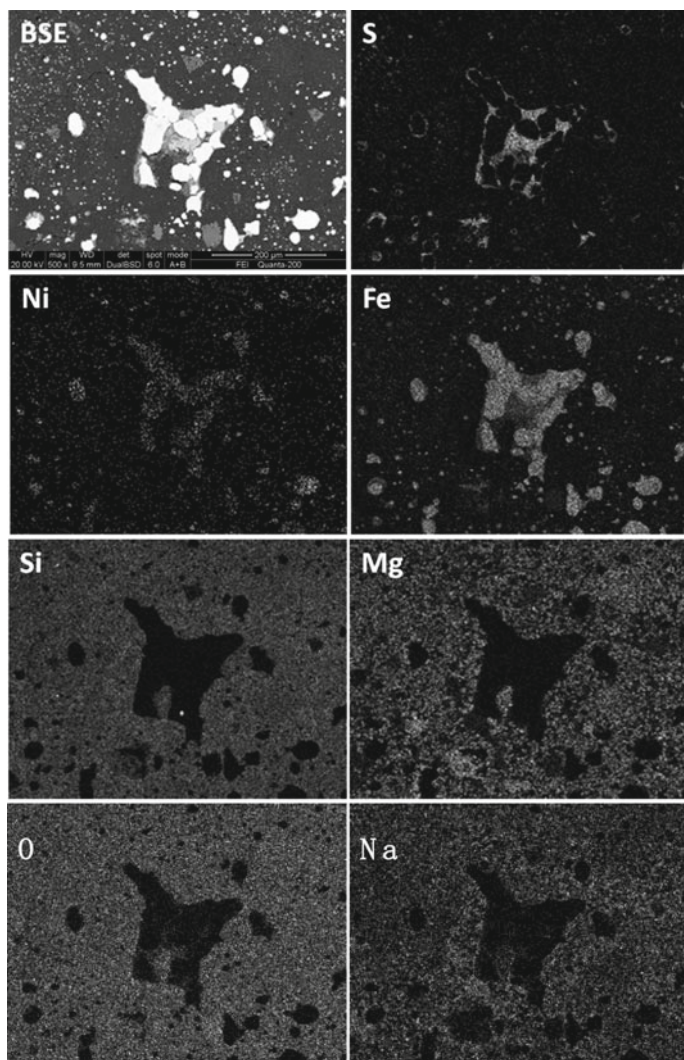


Fig. 2.39 SEM images of laterite ore after reductive roasting in the presence of sodium sulfate, reprinted from Ref. [8], copyright 2022, with permission from Taylor & Francis

According to Fig. 2.39, Ni in the reduced pellets was almost distributed in the zone of Fe, forming solid solution of ferronickel alloy, while a part of Fe had the consistent distribution with S, in the form of FeS. The ferronickel grains were scattered in the matrix of sodium, magnesium and silicon compounds. As a result, the formation of liquid phase was mainly resulted from FeS.

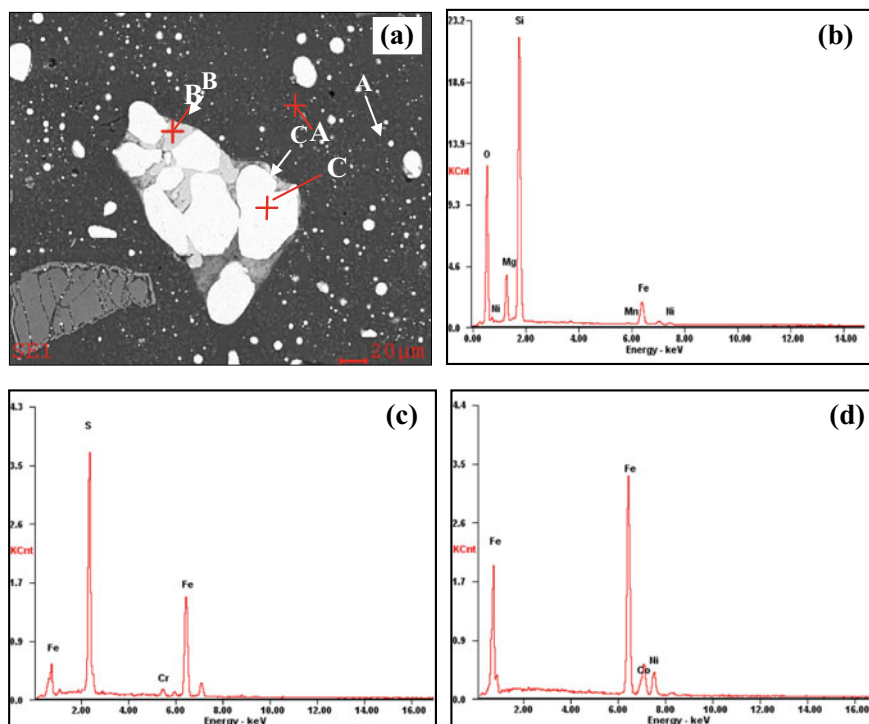


Fig. 2.40 SEM–EDS analysis of laterite ore after reductive roasting in the presence of sodium sulfate: **a** image of backscattered electron and EDX results, **b** Point A in Figure (a), **c** Point B in Figure (a), and **d** Point C in Figure (a)

2.3.4 Growth Mode of Ferronickel Particles

Besides sulfidation product of ferric oxide (FeS), the sulfidation product of nickel oxide, NiS, also exists in reduction system of laterite ore added with sodium sulfate. NiS is not stable at high temperature and will break into Ni_3S_2 and S_2 through heating under inert or reducing atmosphere. The above sulfidation products easily react with metallic Fe and Ni to form low-melting point compound. According to state diagram of the Ni– Ni_3S_2 –FeS–Fe system in Fig. 2.41 [14], the findings can be summarized as follows.

- (1) Four components (Fe–FeS– Ni_3S_2 –Ni) completely dissolve with each other above liquid phase.
- (2) According to isothermal of state diagram, the top melting point is located around the Fe–Ni side, while the bottom melting point is located around E_2 . That is to say, the higher the metallization degree of the system is, the higher the melting point will be. On the contrary, the higher the content of Ni_3S_2 in system is, the lower the melting point will be.

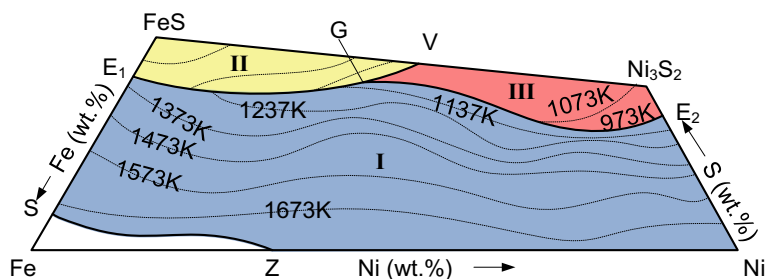


Fig. 2.41 State diagram of the Ni-Ni₃S₂-FeS-Fe system [15]

- (3) The state diagram is divided into three primary crystal zones by two binary eutectic lines E₁-G and E₂-G and a crystalline transition line V-G, i.e., I—Fe-Ni, II—FeS, III—(FeS)₂·Ni₃S₂-Ni₃S₂-Ni solid solution. Zone I occupies the majority of state diagram. As system temperature constantly declines, Fe-Ni will be precipitated.

The sulfidation degree of nickel was obviously lower than that of iron and the nickel content in laterite ore was lower than iron. Then, the influence of Fe-FeS system on the growth features of ferronickel grains was investigated. According to binary phase diagram of Fe-S system (Fig. 2.42), FeS and Fe will form low-melting point compound (Melting point of FeS: 1188 °C; melting point of Fe: 1608 °C; melting point of Fe-FeS: 985 °C). When iron completely transforms into metal Fe and FeS in the reduction process of laterite ore, the S/Fe mass ratio could be calculated in the presence of sodium sulfate. The S/Fe mass ratio with the addition of 20 wt% sodium sulfate is 20.4%, corresponding to red dotted line, as shown in Fig. 2.42. At this moment, the area with temperature higher than the temperature at eutectic point (985 °C) serves as a co-existing area for solid-state metallic iron and liquid phase. The solidification process of melt body follows the eutectoid transformation rules and therefore the structure of Fe wrapped by FeS can be finally formed.

According to the evolution characteristics of growth and occurrence correlation between Fe-Ni and FeS in the reduction process of laterite ore (Fig. 2.43), when temperature was higher than 1000 °C, the shape of ferronickel grains had changes due to the presence of liquid phase and the surface edges disappeared.

In conclusion, the formation of Fe-FeS eutectic point compound resulted in decline of softening temperature of the mixed laterite ore-sodium sulfate system. At higher temperatures, more Fe-FeS liquid phase was formed. Because the mass transfer speed of liquid phase was far larger than that of solid phase, the formation of liquid phase would accelerate the overall mass transfer process to provide channel for diffusion of iron, precipitation and aggregation of small particles to large grains. These factors promoted aggregation and growth of ferronickel alloy grains [16].

In the presence of sodium sulfate, the reduction process of laterite ore was accompanied by generation of microdomain liquid phase due to the formation of eutectic point compound Fe-FeS. When the liquid phase existed, especially in the early stage

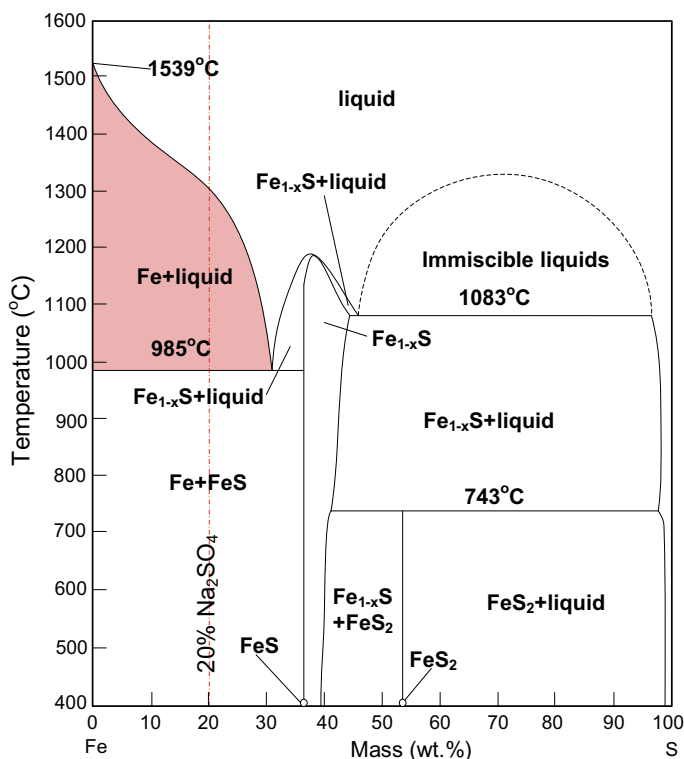


Fig. 2.42 Binary phase diagram of the Fe–S system, reprinted from Ref. [8], copyright 2022, with permission from Taylor & Francis

of dissolution–precipitation, the grains had heterogeneous position changes and the grain boundary might move to the negative direction of center of curvature under chemical driving force in the form of liquid phase film. The three basic grain combination mechanisms (Fig. 2.44) were proposed as follows: the grain boundary at neck sweeping to direction of small particle; the small particles dissolving to liquid phase and then precipitating on surface of large grain; migration of liquid phase film for grain boundary. The above three mechanisms were completely consistent with the occurrence features of ferronickel grains and FeS observed in this test. As a result, the theory of liquid-phase sintering for powder sintering well explained the growth of ferronickel grains in the mixed laterite ore-sodium sulfate system.

According to theory of liquid-phase sintering, the growth and aggregation mechanisms of ferronickel grains in the mixed laterite ore-sodium sulfate system after reduction could be determined, as shown in Fig. 2.45. There were three stages of liquid-phase sintering [17].

At proper sintering temperatures, the formed liquid phase would fill in pores. As liquid phase flew, the grains would slide, rotate and rearrange and the sintered body had rapid densification. This was the first stage of liquid-phase sintering, i.e., grain

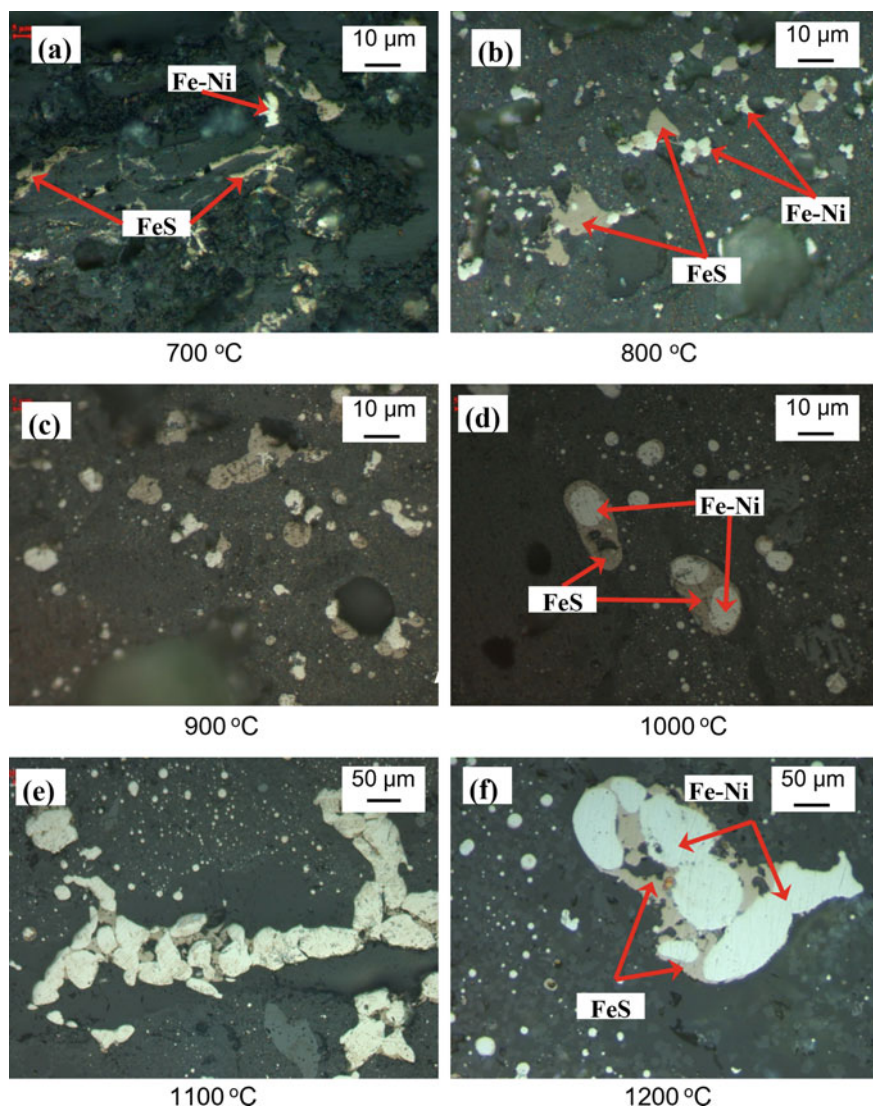


Fig. 2.43 Evolution of growth and occurrence correlation between Fe–Ni and FeS in the reduction process

rearrangement stage. The liquid phase only flew in pores to promote sliding, rotation and rearrangement of grains. It could be regarded as the first rearrangement of grains. Besides, the liquid phase permeated and corroded along internal grain boundaries and then separated the single grain into smaller grains, denoting the second rearrangement of grains.

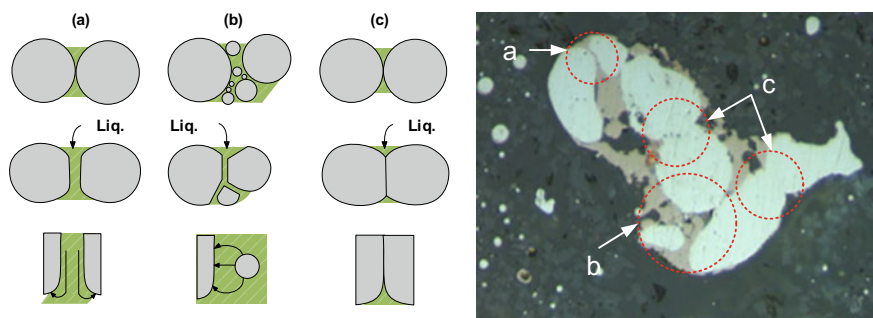
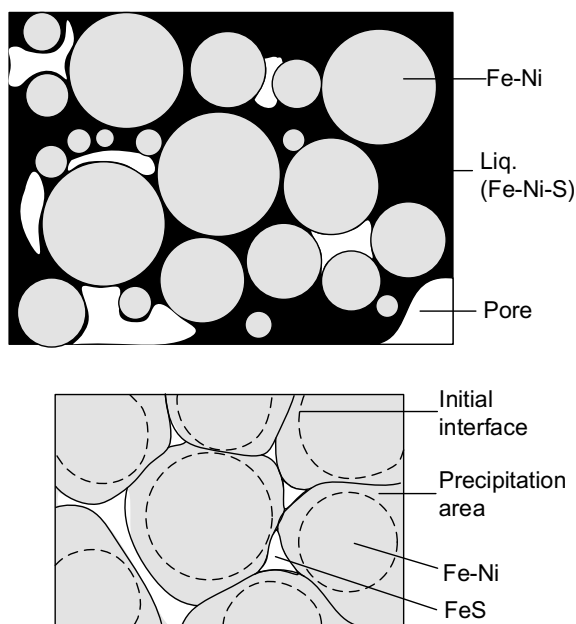


Fig. 2.44 Reforming and dissolution–precipitation of grains in liquid-phase sintering process and neck growth model

Fig. 2.45 Growth and aggregation mechanisms of ferronickel grains in the mixed laterite ore-sodium sulfate system after reduction



In the second stage, the dissolution–precipitation took place. In this stage, the diffusion process was intensified. The corner edges, slight bulge of large grain and small grains dissolved in liquid phase. When the concentration of solid phase in liquid phase exceeded saturation, precipitation would occur on the surface of large grains again.

In the third stage, the solid-phase sintering occurred. The neck and grains increased continuously.

The above three stages of liquid-phase sintering might overlap or change with temperature, atmosphere and liquid phase content. For example, when the liquid phase was not enough, the grain rearrangement would not occur or become obvious,

while the contribution of liquid-phase sintering to grain rearrangement and dissolution and precipitation would greatly increase when there was a high content of liquid phase. When the liquid phase content was about 35%, the grain boundary would rapidly migrate. When the liquid phase content reached 50%, the solid phase grains would grow in the form of combination to form grain boundary framework of solid phase.

2.4 New Process of Preparing Ferronickel Through Selective Solid-State Reduction-Magnetic Separation and Its Application

The nickel grade in laterite ore is low and nickel mainly exists in goethite and serpentite in the form of isomorphism. The nickel reduction degree is usually low in solid-state reduction process and the newly-generated ferronickel particles are small. Therefore, it is difficult to separate them from gangue minerals such as silica and magnesia. Besides, the nickel recovery and Ni–Fe product quality are low.

Depending on sulfidation of sulfidizing reagent, the complete reduction of ferric oxides to metallic iron can be hindered to improve Ni/Fe ratio in the roasting products. On the other hand, in the presence of sodium salt or calcium salt, the structure of serpentite can be destroyed to realize reduction of nickel oxides to the largest extent and improve nickel recovery. By forming metallic iron along with alloying metallic nickel, ferronickel with high nickel content can be beneficiated through magnetic separation.

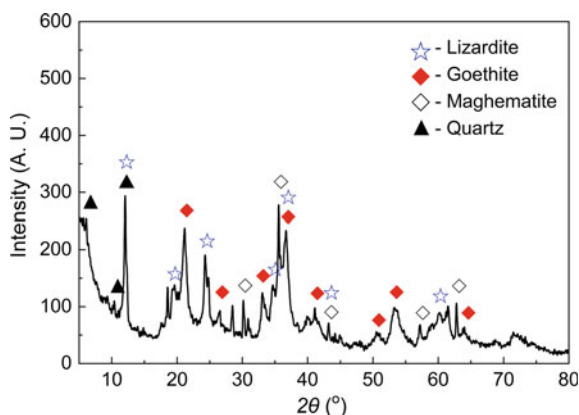
Firstly, the lab-scale reduction test was performed to optimize technological process parameters for selective reduction of laterite ore and to build technological prototype for preparing ferronickel. The technological process and technical parameters through the pilot-scale test for simulating coal-based direct reduction with “firing model” of rotary kiln and industrial test of coal-based direct reduction in rotary kiln were further investigated.

After drying, laterite ore was crushed and ground to 80% of the particles with size smaller than 0.074 mm and used for lab-scale test and pilot-scale test for simulating coal-based direct reduction with the “firing model” of rotary kiln. Table 2.13 shows the main chemical composition of laterite ore. Figure 2.46 shows its main phase composition.

According to Fig. 2.46, the main minerals in laterite ore included serpentite ((Mg, Fe, Ni)₃Si₂(OH)₄O₅), goethite ((Fe, Ni)OOH), hematite (Fe₂O₃) and quartz (SiO₂).

Table 2.13 Main chemical composition of laterite ore (wt%)

Fe _{total}	Ni	Co	SiO ₂	MgO	Al ₂ O ₃	CaO	Cr ₂ O ₃	Mass loss on ignition
22.1	1.91	0.05	26.49	13.4	4.25	2.04	1.68	13.18

Fig. 2.46 XRD pattern of laterite ore

Due to high contents of MgO and SiO_2 in laterite ore, 13.4% and 26.49%, respectively, this ore belonged to a typical saprolitic type.

According to the results of thermogravimetry–differential scanning calorimetry (Fig. 2.47), there was an endothermic peak of 89 °C, corresponding to the removal of free water. The endothermic peak at 271 °C was resulted from removal of crystal water and the endothermic peak at 597 °C was a result of endothermic removal of water contained in serpentite. The generation of amorphous Mg_2SiO_4 after dihydroxylation of serpentite was exothermic with a peak at 809 °C.

To determine the occurrence states of nickel and iron in laterite ore, the chemical sequence extraction method was used to measure nickel and iron distribution. As shown in Tables 2.14 and 2.15, nickel mainly existed in iron oxides (goethite) in the form of isomorphism, with proportion of 76.84%, and the rest existed in silicate

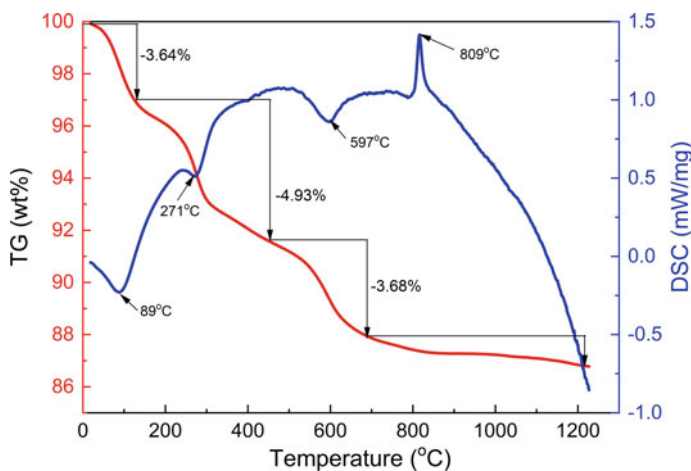
**Fig. 2.47** TG-DSC analysis of laterite ore

Table 2.14 Occurrences of nickel and content distribution

Occurrence	Nickel oxide	Nickel sulphide	Nickel in iron oxide	Nickel in silicate	Total
Nickel content (wt%)	0.2	0.02	1.46	0.23	1.91
Distribution (%)	10.53	1.05	76.84	11.58	100

Table 2.15 Occurrences of iron and content distribution

Occurrence	Goethite	Sulfide	Martite	Iron in silicate	Total
Iron content (wt%)	14.88	0.33	2.18	4.71	22.1
Distribution (%)	67.35	1.48	9.86	21.31	100

(lizardite) in the form of nickel oxide. Iron mainly existed in goethite, with proportion of 67.35%, followed by silicate and martite.

The anhydrous sodium sulfate (Na_2SO_4) was used as sulfidizing reagent. It was ground with particle size smaller than 0.074 mm and mixed with laterite ore with a certain mass ratio for pelletizing. The lignite was used as reducing agent for reduction after being crushed. The reaction performance of the coal complied with coal requirements for direct reduction. Table 2.16 shows the proximate analysis of lignite and its ash fusion point.

The selective reduction of laterite ore was conducted in a vertical resistance furnace equipped with a DWK–702 precision temperature controller (Fig. 2.7). The reduction was performed in a stainless-steel tank with inner diameter of 20 mm loaded in the furnace. The reducing gas was 99.5% CO mixed with high-purity nitrogen (99.999%) as protective gas during reduction, with the total gas flow rate of 200 L/h controlled by a flowmeter.

Figure 2.48 shows the workflow of the small-scale test in lab for direct reduction of laterite ore.

Sodium sulfate and laterite ore with 80% of the particles having size smaller than 0.074 mm were weighed according to the required mass ratio and mixed before pelletizing. The obtained green pellets were dried for 2 h in a constant-temperature drying oven at 110 °C. Before test, 50 g of coal was put into the bottom of stainless-steel tank ($\Phi 60 \text{ mm} \times 150 \text{ mm}$). Then, about 40 g of dried pellets were then put into the tank and then covered with excessive coal. The tank was put into the vertical resistance furnace with the inner diameter of 70 mm for reduction (Fig. 2.49). After reduction, the pellets were taken out [13, 18].

The reduced pellets were crushed with particle size of 100% smaller than 1 mm in advance and then were weighed. 20 g of the pellets were transferred for ball grinding mill (Wuhan Locke Grinding Equipment Manufacturing Co., Ltd., RK/ZQM LCD Smart Ball Grinding Mill) and then was used for magnetic separation in the small-scale wet magnetic separation tube after wet grinding.

Table 2.16 Proximate analysis and ash fusion point of lignite

S	Proximate analysis (wt%)			Ash fusion point (°C)				Calorimetry (MJ·kg ⁻¹)
	Moisture	Ash	Volatile	Fixed carbon	Deformation	Softening	Hemispherical	
0.24	4.63	6.46	37.54	55.72	1240	1260	1280	25.44

Fig. 2.48 Flowsheet of the lab-scale test of direct reduction-magnetic separation

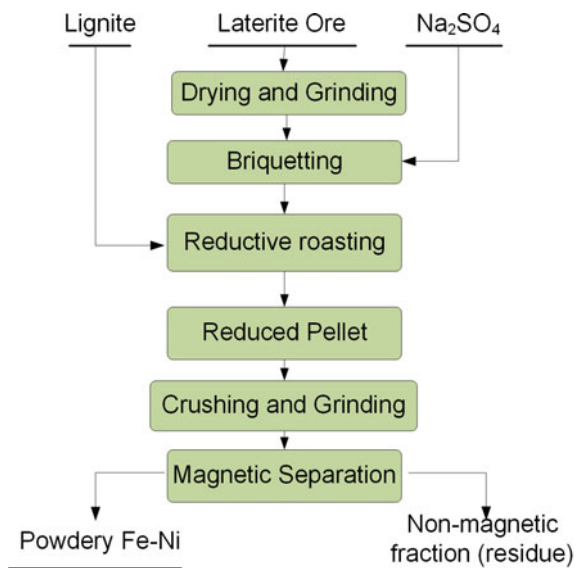
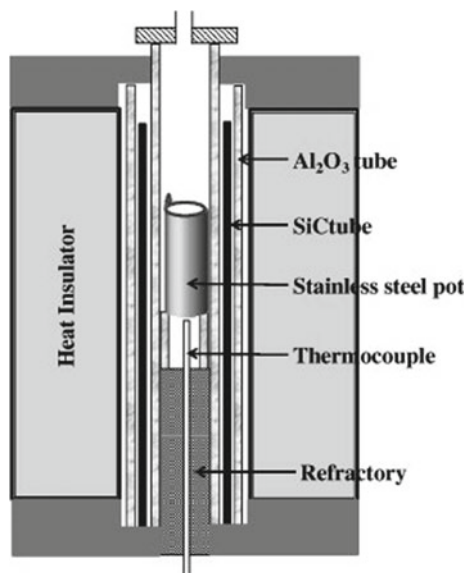


Fig. 2.49 Schematic illustration of the vertical resistance furnace



The thermogravimetry–differential scanning calorimetry (TG-DSC) analysis of raw materials was conducted in a TG analyzer in the temperature range 30–1400 °C, with heating rate of 10 °C/min, atmosphere of nitrogen and gas flow rate of 20 mL/min. An X-ray diffractometer was used to measure phase composition of the materials. An optical microscope was used to observe microstructures of

reduction products and an environmental scanning electron microscope was used to analyze distribution states of main elements in the reduction products.

Main evaluation indexes

The Ni and Fe grade and recovery in the magnetic product obtained from magnetic separation were considered as evaluation indexes. They could be calculated using the equation as follows.

$$\gamma = \left(\frac{m_0 \times \beta}{m_1 \times \alpha} \right) \times 100\% \quad (2.20)$$

where

- γ recovery percentage of nickel or iron (%);
- α nickel or iron grade in the reduced pellets (wt%);
- β nickel or iron grade in the magnetic product (wt%);
- m_1 mass of ground roasting pellets (g);
- m_0 ferronickel mass of magnetic product (g).

2.4.1 Main Technological Parameters

2.4.1.1 Dosage of Sodium Sulfate

Figure 2.50 shows the effects of addition of sodium sulfate on the magnetic separation indexes of reduced pellets of laterite ore under the conditions of reduction temperature of 1100 °C, reduction time of 60 min, grinding fineness of 90 wt% of the particles < 43 μm , and magnetic field intensity of 1000 Gs.

Without the addition of sodium sulfate, the results of magnetic separation were not ideal. The nickel grade and iron grade in the magnetic concentrate were 2.33 wt% and 62.79 wt%, respectively, while the recovery was only 56.97% for nickel and 65.75% for iron.

The addition of sodium sulfate obviously improved the separation indexes of reduced pellets of laterite ore. Within the addition range of 0–20 wt% sodium sulfate, the nickel grade and recovery in the magnetic concentrate increased with the addition of sodium sulfate. Compared with the magnetic separation indexes obtained by reduction without the addition of sodium sulfate, adding 20 wt% sodium sulfate led to increase of nickel grade from 2.33% to 9.48% and increase of nickel recovery from 56.97% to 83.02%. The metallization degree of iron in reduced pellets declined constantly from 79.61% to 59.70%, while the iron grade in the magnetic concentrate continuously increased from 62.79 to 79.30%.

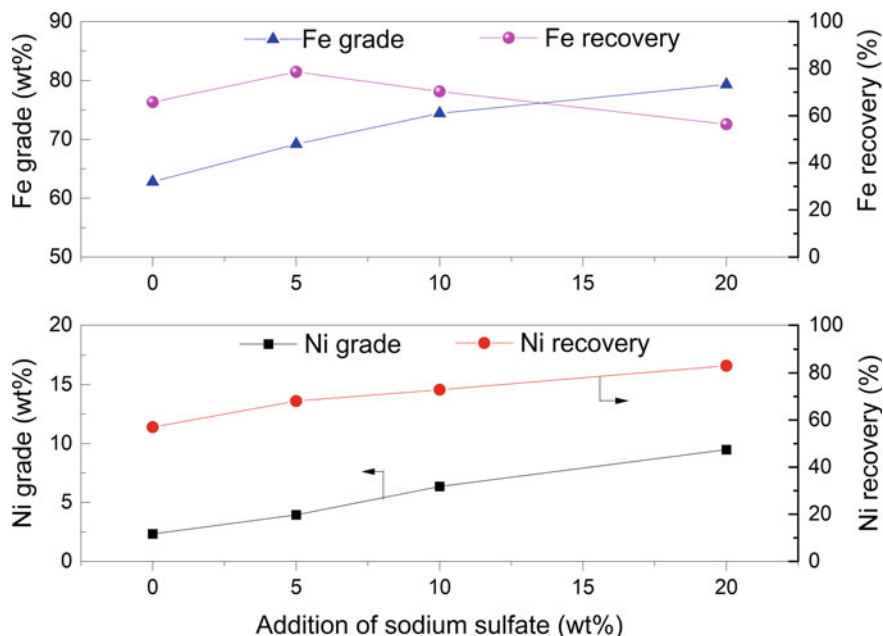


Fig. 2.50 Effects of addition of sodium sulfate on the magnetic separation indexes of reduced pellets of laterite ore by fixing the reduction temperature of 1100 °C, reduction time of 60 min, grinding fineness of 90% < 43 μm , and magnetic field intensity of 1000 Gs

2.4.1.2 Reduction Temperature

Figure 2.51 shows the effect of reduction temperature on reductive roasting-magnetic separation within the temperature range 800–1200 °C without the addition of sodium sulfate. The nickel and iron grade and recovery in the magnetic concentrate increased with reduction temperature. The recoveries of nickel and iron in the magnetic concentrate at 1200 °C were 84.7% and 96.8% respectively, but the nickel and iron grades were only 2.68 wt% and 73.24 wt%, respectively.

In the presence of 20 wt% sodium sulfate, the indexes magnetic separation for reduced pellets improved greatly, as shown in Fig. 2.52. When the reduction temperature increased from 800 to 1100 °C, the nickel and iron grades in the magnetic concentrate, respectively, increased from 7.08 wt% and 69.3% to 9.48 wt% and 79.3%, while the corresponding nickel and iron recoveries, respectively, increased from 25.81% and 19.96% to 83.01% and 56.36%. When the reduction temperature further rose to 1200 °C, the nickel and iron recoveries increased slightly, while the nickel grade slightly declined from 9.48 wt% to 9.25 wt%.

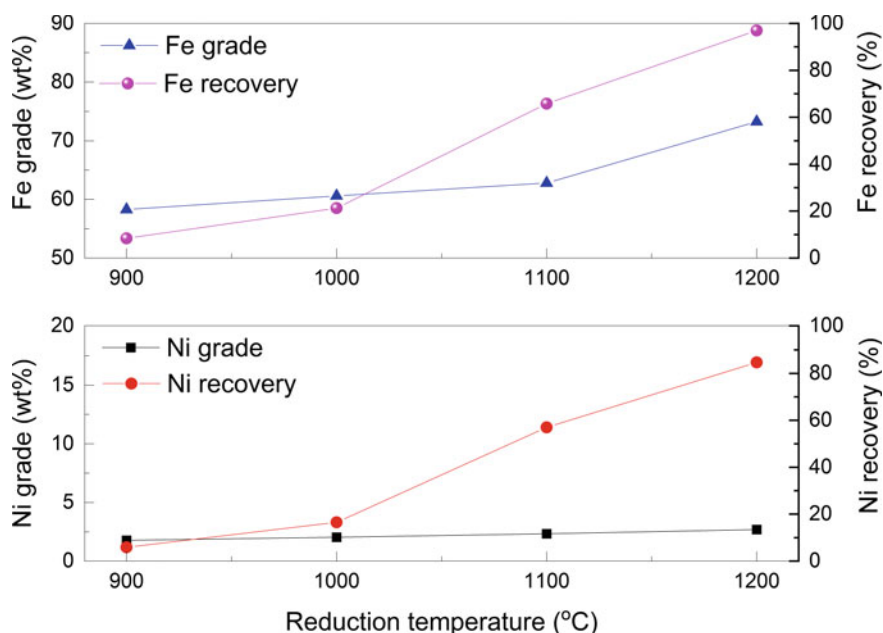


Fig. 2.51 Effect of reduction temperature on the magnetic separation indexes of reduced pellets of laterite ore without the addition of sodium sulfate by fixing the reduction time of 60 min, grinding fineness of 90% < 43 μm , and magnetic field intensity of 1000 Gs

2.4.1.3 Reduction Time

Figures 2.53 and 2.54 show the effects of roasting time on reductive roasting-magnetic separation for laterite ore at reduction temperature of 1100 °C. In the absence or presence of sodium sulfate, increasing reduction time promoted reductive roasting-magnetic separation. With the addition of 20 wt% sodium sulfate, when roasting time increased from 15 min to 30 min, the nickel and iron grades and recoveries increased greatly. When the time increased to 120 min, the nickel grade tended to decline, while the nickel recovery, iron grade and recovery increased slightly. As a result, the appropriate time for reduction roasting was about 60 min. At this moment, the nickel and iron grades were 9.48 wt% and 79.3 wt% in the magnetic products and their recoveries were 83.0% and 56.36%, respectively.

2.4.1.4 Feed Fineness

The reduced pellets of laterite ore added with 20 wt% sodium sulfate were considered as objects (reduction temperature 1100 °C and reduction time 60 min) to verify effects of grinding fineness of reduced pellets on magnetic separation with the magnetic field intensity of 1000 Gs, as shown in Fig. 2.55.

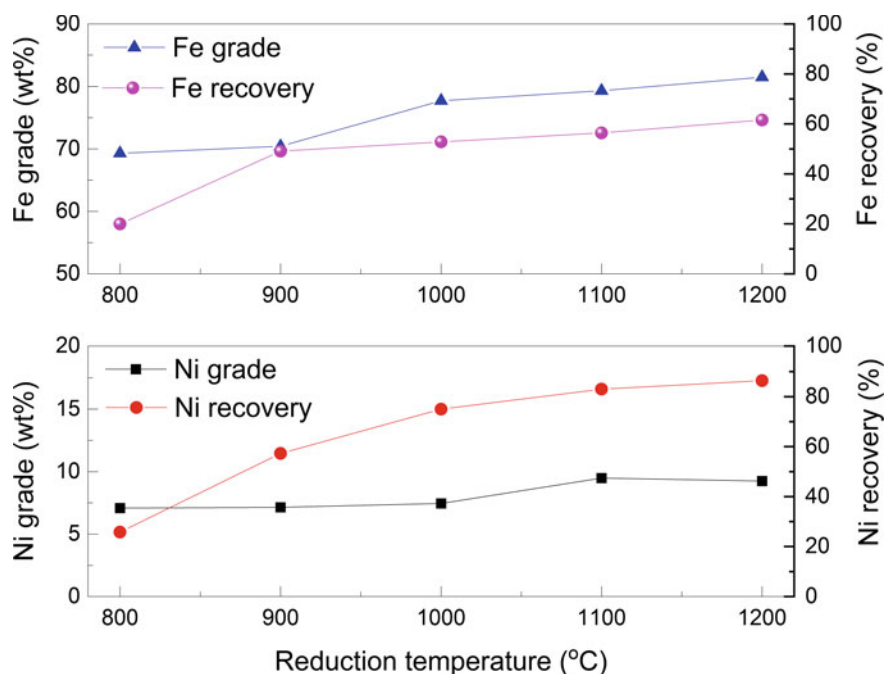


Fig. 2.52 Effects of reduction temperature on the magnetic separation indexes of reduced pellets of laterite ore with the addition of sodium sulfate by fixing the reduction time of 60 min, grinding fineness of 90% < 43 μm , and magnetic field intensity of 1000 Gs

According to Fig. 2.55, the grinding fineness had certain effects on nickel and iron grades of magnetic separation products. Within the test range of grinding fineness, as the content of particles with size of $\sim 43\ \mu\text{m}$ size increased, the nickel and iron grade would slightly rise, but the recovery of iron constantly declined because small grinding fineness would result in argillization and increase of difficulty in separating ferronickel from gangue minerals. Regarding energy consumption for ore grinding and performance of magnetic separation, the suitable grinding fineness was 90% of the particles smaller than 43 μm .

2.4.1.5 Magnetic Field Intensity

The reduced pellets of laterite ore added with 20 wt% sodium sulfate (reduction temperature of 1100 $^{\circ}\text{C}$ and reduction time of 60 min) were used to verify effect of magnetic field intensity on magnetic separation (grinding fineness of 90% smaller than 43 μm), as shown in Fig. 2.56.

As magnetic field intensity increased, although the metal recovery increased, the nickel and iron grades in magnetic products tended to decline slightly. The higher magnetic field intensity made other excessive low-magnetic or non-magnetic gangue

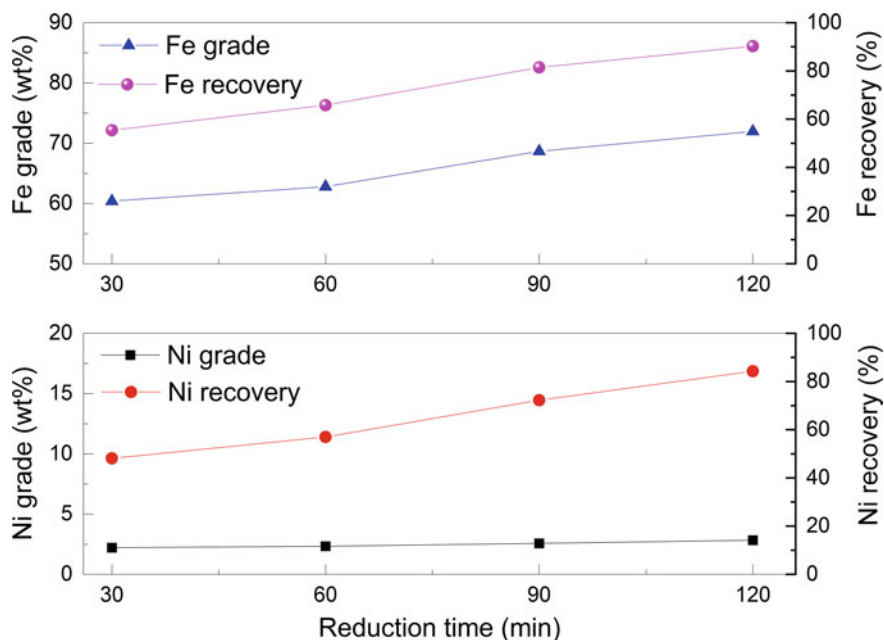


Fig. 2.53 Effects of reduction time on the magnetic separation indexes of reduced pellets of laterite ore without the addition of sodium sulfate by fixing the reduction temperature of 1100 °C, grinding fineness of 90% < 43 μm , and magnetic field intensity of 1000 Gs

minerals aggregate with magnetic mineral particles, resulting in decreases of nickel and iron grades in the magnetic concentrate. In view of nickel grade and recovery, the proper magnetic field intensity was 1000 Gs.

2.4.1.6 Properties of Magnetic Separation Products

Figures 2.57 and 2.58 show the XRD patterns and morphologies of magnetic products.

According to reductive roasting-magnetic separation indexes of laterite ore, adding sodium sulfate improved the performance of reductive roasting-magnetic separation. The optimal process conditions were roasting temperature of 1100 °C, roasting time of 60 min, addition of 20 wt% sodium sulfate, grinding fineness of 90 wt% of the particles smaller than 0.043 mm and magnetic field intensity of 1000 Gs. The nickel and iron grades in magnetic concentrate under the above conditions were 9.48 wt% and 79.30 wt% respectively, and the recoveries of nickel and iron reached 83.02% and 56.36%, respectively.

According to Figs. 2.57 and 2.58, the improvement of reductive roasting-magnetic separation in the presence of sodium sulfate could be verified. After reduction for 60 min at temperature of 1100 °C with the addition of 20 wt% sodium sulfate,

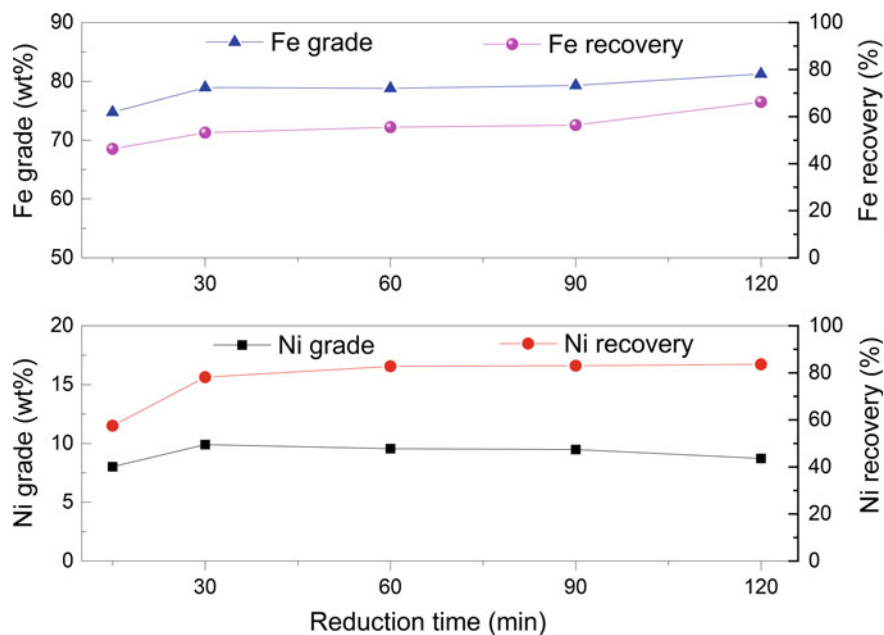


Fig. 2.54 Effects of reduction time on the magnetic separation indexes of reduced pellets with the addition of sodium sulfate by fixing the reduction temperature of 1100 °C, sodium sulfate of 20 wt%, grinding fineness of 90% < 43 μm , and magnetic field intensity of 1000 Gs

metallic nickel and iron solid solution generated from reduction produced magnetic ferronickel alloy, which had effective separation from non-magnetic gangue by magnetic separation (Fig. 2.58b). However, in the absence of sodium sulfate, a part of gangue minerals such as forsterite and enstatite remained in the magnetic product (Fig. 2.57a), while the gangue minerals adhered to ferronickel particles in the form of fine particles. As a result, the effect of monomer separation was not sufficient, resulting in unsatisfactory magnetic separation.

The reduced pellets of laterite ore added with 20 wt% sodium sulfate were selected as objects (reduction temperature 1100 °C and reduction time 60 min) to test main chemical compositions of products from reductive roasting, magnetic products from magnetic separation and non-magnetic materials under the conditions of grinding fineness of 90% smaller than 43 μm and magnetic field intensity of 1000 Gs. Table 2.17 shows the main chemical components and distribution of species of products in the process of reductive roasting-magnetic separation.

According to Table 2.17, Ni and Fe were mainly distributed in magnetic concentrate after magnetic separation, while the contents of other gangue components in the magnetic concentrate such as SiO_2 , MgO and S were low and most of them were enriched in the non-magnetic residue.

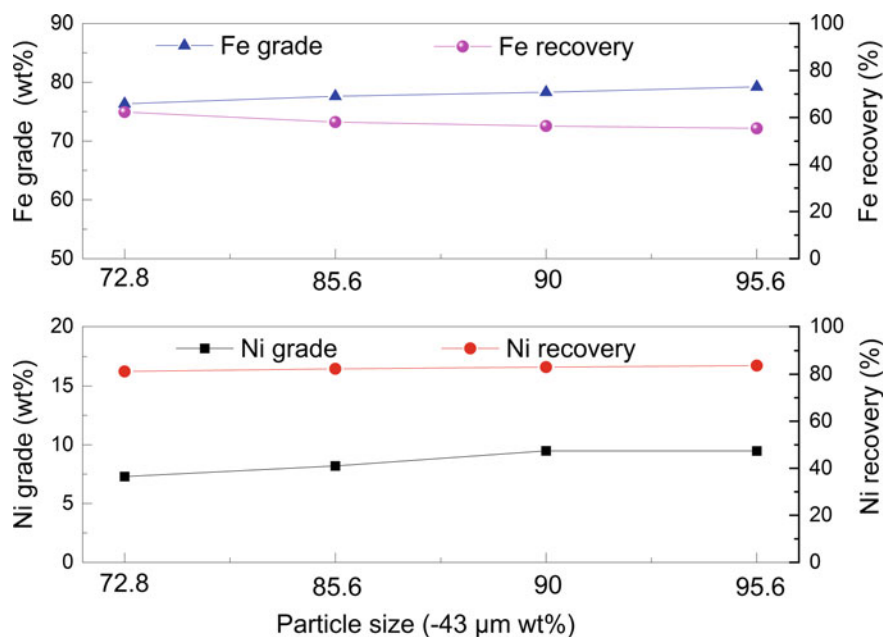


Fig. 2.55 Effects of grinding fineness on the magnetic separation indexes of reduced pellets for laterite ore by fixing the reduction temperature of 1100 °C, reduction time: 60 min, and magnetic field intensity of 1000 Gs

2.4.2 Pilot-Scale Test of Direct Reduction Within “Firing Model” of Rotary Kiln

Based on the small-scale test in lab, a pilot-scale test for simulating coal-based direct reduction in rotary kiln was further conducted. The main technological parameters included percentage of laterite ore pellets/coal, percentage of coal feeding, feeding temperature, heating rate, reduction temperature, and reduction time.

The raw materials for pilot-scale test using so called “firing model” were the same as those for small-scale test in lab. The coal-based rotary kiln direct reduction (Fig. 2.59) was performed in a self-made $\Phi 1000 \times 550$ mm “firing model” using natural gas as fuel.

The green pellets of laterite ore (addition of sodium sulfate: 20 wt%) were firstly dried and put into rotary kiln together with lignite for reduction at high temperature. After roasting at constant temperature, reduced pellets were taken out from the kiln and put into a vessel with coverage of coal. Figure 2.60 shows the workflow of the pilot-scale test for coal-based direct reduction.

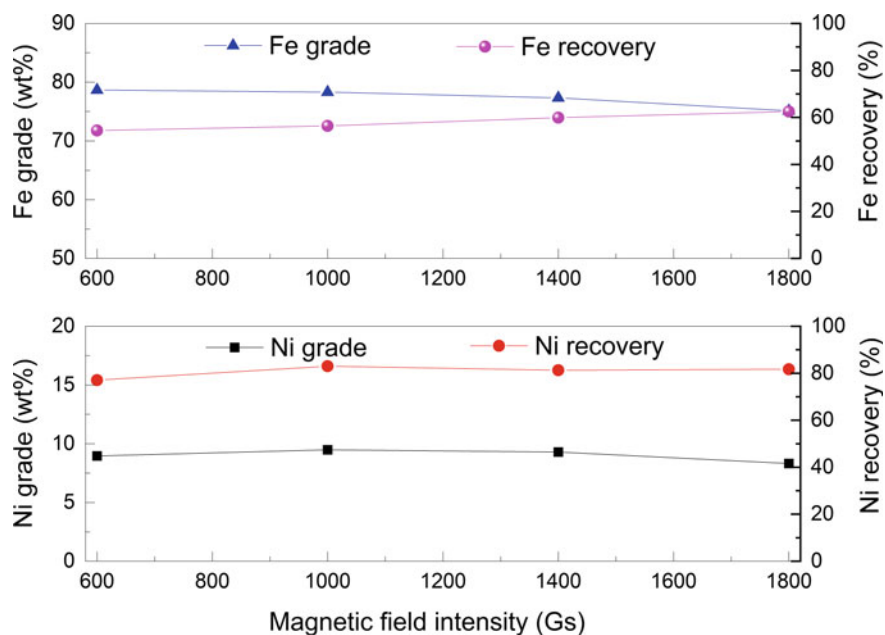


Fig. 2.56 Effects of magnetic field intensity on the magnetic separation of reduced pellets for laterite ore by fixing reduction temperature of 1100 °C, reduction time: 60 min, and grinding fineness of 90% < 43 μm

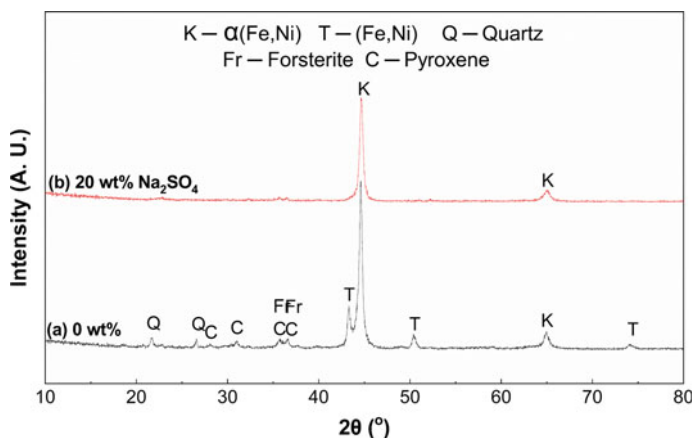


Fig. 2.57 XRD patterns of magnetic concentrate: **a** no sodium sulfate and **b** addition of 20 wt% sodium sulfate

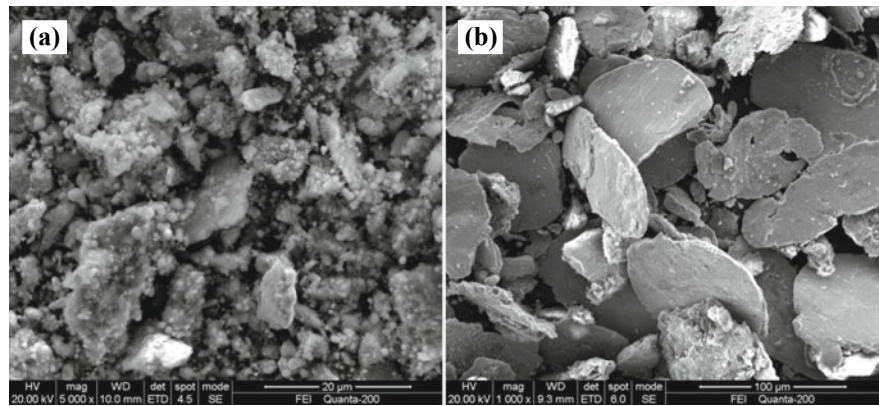


Fig. 2.58 Morphologies of magnetic concentrate: **a** no sodium sulfate and **b** addition of 20 wt% sodium sulfate

Table 2.17 Main chemical components and distribution of species of products in the process of reductive roasting-magnetic separation (%)

Samples	Fe	Ni	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	S
Roasted ore	29.15	2.36	31.77	2.42	1.80	15.10	7.22	3.88
Magnetic materials	79.30	9.48	4.49	0.77	1.12	2.19	1.05	0.51
Distribution	58.20	83.80	3.25	7.26	10.00	2.70	3.73	2.47
Non-magnetic fraction	18.30	0.47	36.38	2.69	2.83	20.07	9.53	4.97
Distribution	41.80	16.20	96.75	92.74	90.00	97.30	96.27	97.53

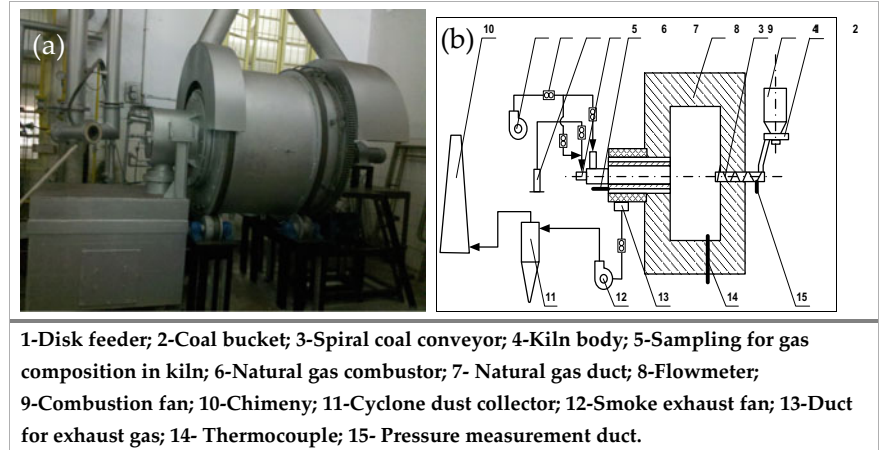


Fig. 2.59 “Firing model” simulating apparatus for rotary kiln: **a** photo and **b** structural illustration

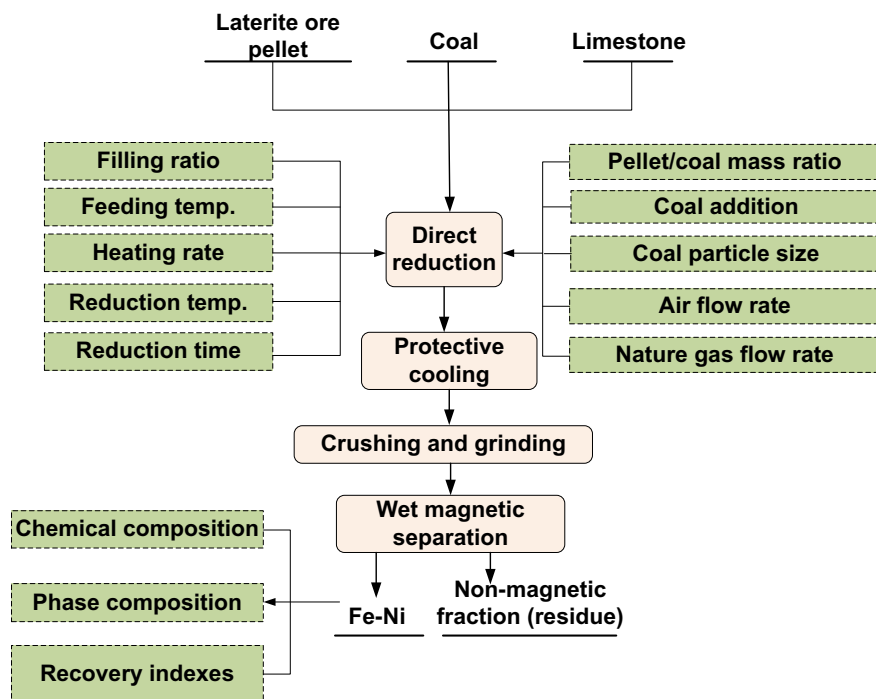


Fig. 2.60 Workflow of pilot-scale test for simulating direct reduction with the “firing model” of rotary kiln

2.4.2.1 Pellet/Coal Mass Ratio

Increasing reducing agent in the process of reduction in rotary kiln would increase reaction interface to improve contact conditions between ores and reducing agent, strengthening reducing atmosphere to accelerate process of reduction reaction. In practical operation, to ensure reduction performance, the dosage of reducing agent is usually larger than theoretical value.

The effects of pellet/coal mass ratio on indexes of reduction-magnetic separation of laterite ore were investigated. The test conditions included pellets of 20 kg, continuous feeding of coals at kiln tail and middle part of kiln upon percentage of 5, heating range of 900–1080 °C for rotary kiln, heating rate of 4.5 °C/min, reduction temperature of 1080 °C, and reduction time of 60 min. Table 2.18 shows the test results.

As the proportion of reduction coal increased, the Fe metallization degree in reduced pellets gradually increased. Under the conditions of the pellets/coal mass ratio of 2/3, Fe metallization degree reached 70.67% and the Ni grade in magnetic concentrate reached 8.86%. The Fe grade was 85.42% and Fe recovery was 67.02%. The Ni recovery was 89.41%. Further increasing the proportion of coal

Table 2.18 Effects of pellet/coal mass ratio on indexes of reduction-magnetic separation

Pellet/coal mass ratio	Fe metallization degree of reduced pellets (%)	Magnetic concentrate (%)			
		TNi	TFe	Ni recovery	Fe recovery
1:1.2	65.26	7.49	79.44	81.50	62.96
1:1.5	70.67	8.86	85.42	89.41	67.02
1:2.0	73.95	8.98	87.09	90.83	69.25

would improve index of reduction-magnetic separation. However, excessive coal would undoubtedly increase production cost and decline production efficiency.

2.4.2.2 Reduction Temperature

Increasing reduction temperature would accelerate gasification and reduction reaction of ferric oxides in rotary kiln, but the maximum operating temperature should be determined based on softening temperature of raw materials and softening property of ash content of coal. Generally, the maximum operation temperature is lower than softening temperature of raw materials and ash by 100–150 °C to prevent formation of eutectic point compound due to the presence of ash and ferric materials, resulting in cementation among iron-containing materials or with reactor wall.

The effects of reduction temperature on the indexes of reduction-magnetic separation were investigated under the conditions of pellets of 20 kg, pellets/coal mass ratio of 2/3, continuous feeding of coals at tail and middle part of kiln upon 5%, heating range from 900 °C to target temperature for rotary kiln, heating time of 40 min and reduction time of 60 min at target temperature.

As the reduction temperature increased, the Fe metallization degree of pellets and magnetic separation index gradually increased. At 1050 °C, the metallization degree reached 68.05%; the iron and nickel grades in concentrate were 83.76 wt% and 8.51 wt%, respectively. The Fe and Ni recoveries were 64.76% and 85.66%, respectively. When the reduction temperature further rose to 1080 °C, the Fe metallization degree reached 70.67%. The iron and nickel grades in concentrate were 85.42 wt% and 8.86 wt%, respectively. The Fe recovery was 67.03% and the Ni recovery was 89.41% (Table 2.19).

Table 2.19 Effects of reduction temperature on indexes of reduction-magnetic separation

Reduction temperature (°C)	Fe metallization degree of reduced pellet (%)	Magnetic concentrate (%)			
		TNi	TFe	Ni recovery	Fe recovery
1000	62.41	7.54	78.41	76.45	58.75
1020	65.86	8.04	81.81	82.07	60.46
1050	68.05	8.51	83.76	85.66	64.76
1080	70.67	8.86	85.42	89.41	67.02

Table 2.20 Effects of reduction time on the indexes of reduction-magnetic separation

Reduction time (min)	Fe metallization degree of reduced pellet (%)	Magnetic concentrate (%)			
		TNi	TFe	Ni recovery	Fe recovery
60	68.05	8.51	83.76	85.66	64.76
90	72.72	8.54	85.03	86.89	68.20
120	74.45	8.43	87.45	88.67	70.81

2.4.2.3 Reduction Time

The increase of reduction time had great effects on metallization degree of pellets. Increasing reduction time allowed reducing gas to sufficiently participate in reduction reaction to improve metallization of pellets.

The effects of reduction time on the indexes of reduction-magnetic separation were investigated under the conditions of pellets of 20 kg, pellets/coal mass ratio of 2/3, continuous feeding of coals at tail and middle part of kiln upon percentage of 5, heating range of 900–1050 °C for rotary kiln, heating rate of 3.75 °C/min and reduction temperature of 1050 °C.

As the reduction time increased, the metallization degree of pellets and index of magnetic separation gradually increased. After reduction for 120 min at 1050 °C, the metallization degree reached 69.45%. The iron and nickel grades in the magnetic concentrate were 87.45 wt% and 8.43 wt%, respectively. The Fe and Ni recoveries were 70.81% and 88.67%, respectively. In view of huge energy consumption for maintaining high temperature, the appropriate reduction time was 60–90 min (Table 2.20).

2.4.2.4 Heating Rate

As reduction time increased, the metallization degree of pellets and indexes of magnetic separation gradually increased. In addition, reduction also occurred in the process of heating of materials in rotary kiln body. Decreasing heating rate would enable reduction of the materials. On the contrary, increasing heating rate complied with thermal regulation of coal-based direct reduction process in rotary kiln.

The effects of heating rate on the indexes of reduction-magnetic separation were investigated. The test conditions included pellets of 20 kg, pellets/coal mass ratio of 2/3, continuous feeding of coals at tail and middle part of kiln upon 5%, heating range of 900–1050 °C for rotary kiln, reduction temperature of 1050 °C and reduction time of 60 min.

As heating rate declined, the Fe metallization degree of pellets and indexes of magnetic separation gradually increased. When the heating rate was 1.25 °C/min in the temperature range 900–1050 °C, after reduction for 60 min at 1050 °C, the Fe metallization degree of roasted pellets reached 75.31%. The iron and nickel grades

Table 2.21 Effects of heating rate on the indexes of reduction-magnetic separation

Heating rate (°C/min)	Fe metallization degree of reduced pellets (%)	Magnetic concentrate (%)			
		TNi	TFe	Ni recovery	Fe recovery
3.75	68.05	8.51	83.76	85.66	64.76
2.5	70.99	8.92	85.41	86.47	65.16
2	72.45	8.61	86.19	88.02	67.75
1.25	75.31	8.48	88.45	90.53	69.90

in the magnetic concentrate were 88.45 wt% and 8.45 wt%, respectively. The Fe and Ni recoveries were 69.90% and 90.53%, respectively (Table 2.21).

2.4.3 Industrial Test of Direct Reduction-Magnetic Separation in Coal-Based Rotary Kiln

Through the small-scale test in lab and pilot-scale tests for simulating direct reduction with “firing model” of rotary kiln, the industrial test based on coal-based direct reduction in rotary kiln was performed using a new-built coal-based rotary kiln ($\Phi 1.6 \times 16$ m). The optimized operating parameters would provide reliable technical support for design of new plant and industrial application [19, 20].

2.4.3.1 Raw Materials and Methods

Laterite ore used for industrial test was different from those used in the small-scale test in lab and pilot-scale test. This raw ore had high-content of water, which had adverse effects on subsequent ore grinding, agglomeration and reductive roasting. For this reason, the crystal water and drying were removed firstly.

Table 2.22 shows the main chemical composition of laterite ore after crushing, drying and removal of crystal water. The ore had nickel content of 1.52 wt% and total iron content of 18.82 wt%.

Table 2.22 Main chemical composition of laterite ore used for industrial test after removal of water (wt%)

TFe	Fe ₂ O ₃	FeO	TNi	SiO ₂	MgO
18.85	22.57	2.31	1.52	38.42	18.64
Al ₂ O ₃	CaO	Cr ₂ O ₃	P	S	LOI
3.47	1.71	0.96	0.0093	0.27	5.8

Coal: The coal used for industrial test was the same as that in small-scale test in lab and pilot-scale test for simulation with “firing model” of rotary kiln. Table 2.16 shows the physical and chemical properties of coal.

Additive: To strengthen reduction of laterite ore and aggregation and growth of ferronickel grain, sodium sulfate of industrial grade was used as additive.

Binder: The modified corn starch was used as binder for preparing laterite ore briquettes.

Desulfurizing agent: The limestone was added in the process of reductive roasting as desulfurizing agent. Its main chemical component was calcium oxide and its particle size was 5–10 mm.

Figure 2.61 shows the workflow of the industrial test.

Laterite ore powder was mixed with additive and coal with a certain mass ratio in advance (~5%) and then added with a certain percentage of adhesive agent for mixing.

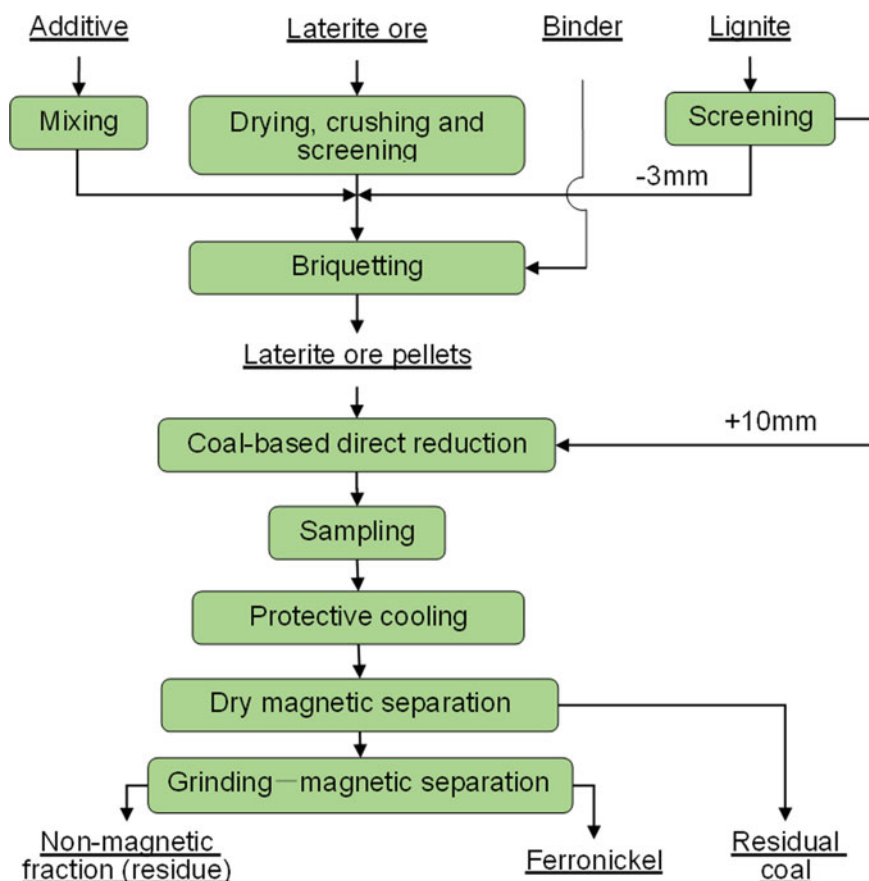


Fig. 2.61 Workflow of the industrial test

Fig. 2.62 Photo of briquetting machine



Fig. 2.63 Photo of dried laterite ore briquettes ($40 \times 40 \times 31$ mm)



Then, the mixture was put into a briquetting machine for briquetting (Fig. 2.62) to produce briquettes with the size of $40 \times 40 \times 31$ mm (Fig. 2.63).

The prepared laterite ore briquettes were used as main raw materials and the size of rotary kiln body was $\Phi 1.6 \text{ m} \times 16 \text{ m}$. Table 2.23 shows the parameters of main equipment. Table 2.24 shows the main operating parameters of rotary kiln. Figure 2.64 shows the photo of the rotary kiln for the industrial test.

The direct reduction for laterite ore briquettes was conducted in rotary kiln. In order to timely understand operation of rotary kiln and reduction state of materials in the kiln, the representative samples obtained during test were put in a special container for natural cooling to room temperature under the condition of air isolation. After separation of residual coal, the cooled samples were used for ore grinding and wet magnetic separation to provide guidance for proper operation of rotary kiln based on reduction and separation indexes.

Table 2.23 Parameters of rotary kiln

Item	Equipment parameters
Total effective length of kiln housing	16 m
Effective inner diameter of rotary kiln	1.15 m
Thickness of fire resistant material for liner of kiln	0.225 m
Inner diameter of steel structure for kiln housing	1.6 m
Effective length-diameter ratio	$16/1.15 = 13.4$
Gradient of installation	2.5% (1.43°)
Length of preheating section	3 m
Length of reduction section	13 m
Fencing for feeding section of kiln tail	Inner diameter (0.7 m), height (0.25 m), top width (0.2 m), gradient (30°)
Fencing for discharge section of kiln head	Inner diameter (0.6 m), height (0.3 m), top width (0.2 m), gradient (30°)
Supporting ring and roller for kiln	2 sets
Fan for kiln housing	2 pieces
Opening position of fan for kiln housing at kiln wall	4.7 and 8.35 m far away from discharge end
High-temperature thermocouple	6 points for measuring temperature in kiln body (position 1: side of feeding head cover; position 2: kiln cylinder of feeding end, near sealing section; position 3: 4 m far away from feeding end; position 4: 7.6 m far away from discharge end; position 5: kiln cylinder of discharge end, near sealing section; position 6: side of discharge head cover)
U-shape differential pressure gauge	Located in side of kiln head cover

2.4.3.2 Test Results

The reduced briquettes were firstly crushed into -1 mm and put into ball mill for wet-grinding after separation of residual coal, and then the drum magnetic separator was used for magnetic separation. After filtering and drying in vacuum drying oven, ferronickel powder was obtained as the magnetic product.

The conditions of grinding-magnetic separation were grinding fineness of 92% lower than $74\ \mu\text{m}$ and magnetic field intensity of 1000 Gs. The materials used for grinding-magnetic separation tests were reduction products from rotary kiln with different sizes (Fig. 2.65). According to Table 2.25, the magnetic separation indexes of #2, 3 and 4 reduced briquettes were better than those of #1. The nickel recovery of #4 was the highest, up to 96.28%; the nickel grade in magnetic product of #3 pellets was the highest, up to 8.75%. Therefore, the reduced briquettes had excellent separation performance.

Table 2.24 Main technical parameters for production and operation of rotary kiln

Item	Technical parameters
Temperature	Temperature of kiln body at feeding end: 950 °C; temperature of kiln body at reduction section: 950–1050 °C; temperature of kiln body at discharge end: 900 °C
Kiln pressure	10–30 mm water column
Kiln speed	0.4–0.5 rpm
Filling ratio of materials	20 wt%
Retention time of materials in kiln	5–6 h
Reduction time of materials	4–5 h
Feeding amount of materials	Laterite ore pellet: 300 kg/h; addition of coal (pellets): 150 kg/h; coal injection: 80 kg/h; limestone: 10–15 kg/h
2 kiln housing machines	90% air volume “ON”; air volume was basically remained when operating conditions of kiln were normal
Coal injection mode	Batch coal injection
Cooling mode	Water quenching for cooling (reduction products were directly conveyed to water quenching pool via double swing valve for discharge)

Fig. 2.64 Coal-based rotary kiln for the industrial test

Table 2.26 shows the main chemical compositions of laterite ore, reduction products, magnetic and non-magnetic products (magnetic concentrate and non-magnetic residue, respectively) from magnetic separation.

The reductive roasting was implemented in the rotary kiln in the presence of additive and ferronickel generated from reduction was effectively separated from non-magnetic gangue through magnetic separation. The content of gangues such as magnesium, silicon and aluminum oxides were obviously lowered, while nickel and iron were enriched significantly.

According to results of the industrial test, the technological process of coal-based direct reduction in rotary kiln followed by physical separation of reduction products was feasible. The steps included preparation of raw materials, coal-based direct reduction in rotary kiln, grinding and magnetic separation of reduced materials.



#1 briquettes (20~30 mm)



#2 briquettes (40~50mm)



#3 briquettes (50~70 mm)



#4 briquettes (>80mm)

Fig. 2.65 Reduced briquettes from rotary kiln for grinding-magnetic separation**Table 2.25** Quality indexes of reduced pellets and magnetic concentrate after magnetic separation of the pellets

Sample	Index of reduced briquettes (%)			Index of magnetic concentrate (%)					
	MFe	TFe	Fe metallization degree	Productivity	TFe	MFe	TNi	Fe recovery	Ni recovery
#1	14.72	9.47	64.33	12.22	82.05	76.46	6.65	68.11	73.21
#2	15.86	10.86	68.47	12.13	87.16	80.47	8.32	66.66	88.53
#3	15.74	10.26	65.18	11.98	89.47	81.5	8.75	66.60	90.37
#4	14.60	11.91	81.50	12.38	86.94	81.44	8.01	75.00	96.28

The optimal conditions for rotary kiln were reductive roasting temperature of 900–1050 °C and retention time in kiln of 5–6 h. For laterite ore with low nickel and iron contents (Ni: 1.52% and TFe: 18.85%), after reductive roasting and grinding-magnetic separation, the ferronickel powder with TFe higher than 86% and Ni content

Table 2.26 Main chemical compositions of laterite ore, reduction products and magnetic separation products (wt%)

Composition	Laterite ore	Roasted ore	Magnetic concentrate	Non-magnetic residue
TFe	18.85	14.6	86.94	4.38
MFe	0.74	11.91	81.44	0.13
Ni	1.52	1.03	8.01	0.08
SiO ₂	38.42	36.13	1.27	41.14
Al ₂ O ₃	3.47	3.14	0.65	3.49
CaO	1.71	3.01	0.47	3.46
MgO	18.64	19.26	1.03	21.69
Na ₂ O	/	7.61	0.43	8.63
Cr ₂ O ₃	0.96	0.51	0.12	0.57
P	0.0093	0.0064	0.028	0.0067
C	0.27	1.5	0.54	1.62
S	0.27	1.52	0.46	1.68

exceeding 8% was obtained. The nickel recovery for reduction product reached 95% and the iron recovery was about 75%. The total content of nickel and iron in ferronickel product was higher than 94% and the Ni/Fe ratio increased from 0.08 in the laterite ore to 0.11 in the ferronickel powder. The contents of Na₂O and harmful elements for steelmaking were lower than 1%, complying with basic requirements for feedstock of steelmaking. The non-magnetic product generated from magnetic separation contained 41.14% SiO₂, 21.96% MgO and 8.63% Na₂O, suitable for further comprehensive utilization.

2.4.4 Comparison Between the New Process and Existing Processes

Through the small-scale experiment in lab, “firing model” pilot-scale test and industrial rotary kiln test, the technological process and equipment were determined, based on the optimal technological parameters of reduction and magnetic separation. The new process of briquetting of mixture of laterite ore and additives—reduction in coal-based rotary kiln—grinding and preparation of ferronickel by magnetic separation has been developed. The new process was implemented in Indonesia in December 2016 (Fig. 2.66) using laterite ore with nickel content of 1.78 wt%. The addition of sodium sulfate was 12% and the operating temperature of rotary kiln was controlled at 900–1050 °C to prepare ferronickel products with nickel content higher than 10.4% and recovery of nickel up to 95.3%. Besides, the Ni/Fe ratio increased from 0.05 in laterite ore to 0.12 in ferronickel powder and the production cost per ton of ferronickel declined by over 30% compared with existing RKEF process.



Fig. 2.66 Main facilities for the new process of preparing ferronickel through coal-based rotary kiln direct reduction-magnetic separation

Table 2.27 shows a comparison of main existing pyrometallurgical processes with the present new process.

Due to bad adaptability for laterite feed, the blast furnace smelting process is applicable to treat the limonite-type laterite ore with high-iron grade and the final product has low nickel content of 3–6% and high contents of impurities such as sulfur and phosphorus. Therefore, it is only used for producing 200 series stainless-steel. Due to high energy consumption, high consumption of coke, increasingly stricter requirements for environmental protection, the blast-furnace smelting process will be restricted.

For the process of RKEF, the proportion of power consumption is about 50% of operating cost and the energy cost of overall process takes up over 65% of the total operating cost. Therefore, abundant electric powder and fuel supply are required.

Due to rigorous production and operating conditions, the Oheyama process of Yakin Kogyo is difficult to be stably controlled and “ring” is easily formed in kiln. Therefore, stable temperature distribution in kiln and feeding speed of pellets are critical factors influencing the stable operation of rotary kiln.

The main advantages of the new process are as follows.

- (1) It has strong adaptation for raw materials. Various kinds of laterite ores can be processed independently.
- (2) Lignite, instead of coke, is used as reducing agent. Excellent reduction and separation effect can be obtained at low reduction temperature i.e., 1000–1100 °C. Compared with expensive metallurgical coke, lignite is featured with large reserves and low cost.
- (3) Short technological process will avoid smelting in blast furnace or submerged arc furnace. Because of no need of coke and low power consumption, it is appropriate to build factory and implement it in remote mines areas. Only one-step reduction is required. The operating temperature can be decreased by over 500 °C compared with those required by blast furnace and electric arc furnace and over 300 °C compared with that of the Oheyama process. Due to short flow-sheet and low energy consumption, the production cost is expected to decline over 30% compared with the existing high-temperature smelting processes.

Table 2.27 Comparison of existing production processes with the present new process for ferronickel-making

Process	Adaptation for laterite feed	Ferronickel products	Main characteristics	Advantages
Blast furnace process	Limonite type (Fe: >35%, Ni: ~1%)	Nickel content of 2–5%, nickel recovery of ~80%, and low ferronickel beneficiation ratio	Two high-temperature steps, advanced agglomeration for sintering machine (1300–1400 °C), and smelting in blast furnace (~1600 °C)	High throughput
Rotary kiln-electric furnace process	Saprolite type (Ni > 1.5%)	Nickel content of 5–8% and nickel recovery of >90%	Two high-temperature steps, reduction in rotary kiln (800–950 °C) and smelting in electric arc furnace (~1600 °C)	Mature technology and high nickel recovery
Oheyama process	Saprolite type (Ni > 2%)	Nickel content of ~20% and nickel recovery of ~90%	One high-temperature step, reduction in rotary kiln and nodulizing (1350–1400 °C), grinding and separation for recovery of ferronickel	Elimination of high-temperature smelting process compared with blast furnace and electric arc furnace method, one-step high-temperature for production of ferronickel, with low energy consumption

(continued)

Table 2.27 (continued)

Process	Adaptation for laterite feed	Ferronickel products	Main characteristics	Advantages
New process	Limonite type and saprolite type (Ni > 1%)	Nickel content of 6–20%, nickel recovery of ~95%, and high ferronickel beneficiation ratio	On high-temperature step, solid-state reduction in rotary kiln (1000–1050 °C), grinding and separation for recovery of ferronickel	Strong adaptation for raw materials, one high-temperature step for production of ferronickel, operating temperature decreased by over 500 °C compared with blast furnace and electric arc furnace and by over 300 °C compared with the nodulizing process, short procedure, low energy consumption, and production cost decreased by over 30% for ferronickel-making compared with nodulizing process

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Chapter 3

Technology of Slag Formation Control in Electric Furnace Smelting of Laterite Ore



Abstract Two-thirds of the global nickel output is produced by the rotary kiln-electric furnace (RKEF) process. Due to the high contents of MgO and SiO₂ and low content of iron in laterite ore, high temperature (~1600 °C) and huge energy consumption (approximately 4000 kW·h/t-ferronickel) are required during the smelting step. This chapter proposes an energy-efficient technique for reducing the smelting temperature and energy consumption by controlling slag formation. The effects of various components on the melting properties of the slag were evaluated by analyzing phase diagrams, generation behaviors of the liquid phase, and viscosity of the slag. Subsequently, a comprehensive regulation of the quaternary basicity [$R_4 = m(\text{CaO} + \text{MgO})/m(\text{SiO}_2 + \text{Al}_2\text{O}_3)$] and FeO content of the slag was proposed, instead of solely controlling the MgO/SiO₂ mass ratio, to facilitate smelting. The high efficiency of the new method was further verified through the lab-scale, pilot-scale and industrial tests, respectively.

Keywords RKEF process · Slag formation · Quaternary basicity · Energy conservation · Laterite ore · Ferronickel

Slag is a multi-component melt of various oxides formed in the most of pyrometallurgical processes. When the ores or concentrates are used as the raw material for smelting, the unreduced oxides and the added fluxes form slag, named smelting slag. In the smelting process, slag plays the key role in ensuring the operation, composition of molten metal, recovery of metal and technical and economic indexes of smelting. These functions are realized by controlling smelting temperature and physicochemical properties of slag [1–3].

Rotary kiln-electric furnace (RKEF) smelting is a typical process of ferronickel production from laterite ore [4–6]. In 2019, the RKEF process produced approximately 15 million tons of ferronickel, which corresponded to two-thirds of the annual nickel output. China and Indonesia contributed nearly 12 million tons of ferronickel in 2019 [7, 8]. In this process, the high-melting-point gangues (10–30 wt% MgO; 20–40 wt% SiO₂) are detrimental to the fusion of feed and the separation of the hot metal during smelting [9, 10]. The main phase in the slag is olivine [(Mg, Fe)₂SiO₄] [11], which requires the furnace to reach a maximum temperature of approximately

1600 °C to ensure the effective separation of molten iron from slag [12, 13], thus consuming nearly 4000 kW·h/t–ferronickel of electric energy during the smelting process [14, 15]. The global energy consumption for ferronickel smelting is over 60 billion kW·h per year. The high–energy consumption of the RKEF process has become the most common concern [16].

Based on production experiences, some plants optimize the laterite ore supply and production process for reducing energy consumption, such as controlling the MgO/SiO₂ mass ratio of mixed feed in the range 0.6–0.7 to reduce smelting temperature, charging the hot calcine from rotary kiln into the electric furnace, and using the hot waste gas of rotary kiln and electric furnace for drying and pre–reducing laterite ore [17–19]. However, compared with the Krupp–Renn process and blast furnace smelting process, the cost of ferronickel production by the RKEF process is still 10–20% higher [20]. Evidently, the energy consumption could be reduced by decreasing the smelting temperature [21].

It is known that high contents of silicon, magnesium, aluminum and other impurities in laterite ore have obvious adverse effects on the softening–melting and dripping properties of slag (such as liquid phase formation and viscosity) in the smelting process [22–24]. Hence, the key to solve this problem is to select a suitable slag composition, which can improve the properties of slag and reduce the smelting temperature. It is of great significance to realize energy conservation and carbon emission reduction in ferronickel production using the RKEF process.

3.1 Phase Diagrams of Slag Systems

Laterite ore is a complex low–grade polymetallic ore. The high contents of silicon, magnesium, aluminum and other components as well as ferrous oxide formed in smelting and calcium oxide mixed as the flux have significant impacts on the properties of the resulting melt. The phase diagram analyses are helpful to clarify the reaction trend of the above components in the high temperature process, especially the phase transformation of the components with different contents, and the influence on the melting properties. The main phase diagrams concerning the CaO–MgO–Al₂O₃–SiO₂–(FeO) slag system were calculated by the FactSage software [25] and the content ranges of low melting point phases and components for different isotherms of each slag system were determined.

3.1.1 MgO–SiO₂–Al₂O₃ Slag System

Based on the characteristics of laterite ore with high contents of silicon and magnesium, the phase diagram of MgO–SiO₂ binary system is first considered and the result is shown in Fig. 3.1. With the MgO content of 0–36 wt%, the main phases are pyroxene (MgSiO₃) and tridymite (SiO₂, s4) at temperatures below 1550 °C.

When the temperature reaches 1550 °C, the enstatite melts into liquid phase and the tridymite transforms into the cristobalite (SiO_2 , s6), which then melts at temperatures above 1680 °C. When the content of MgO is 40 wt% with the MgO/SiO_2 molar ratio of 1, the main phase is enstatite which melts into liquid phase at 1565 °C. As the content of MgO increases to 40–57 wt% and the temperature is lower than 1860 °C, forsterite (Mg_2SiO_4) and MgO are the main phases. Forsterite melts at the temperature of 1860 °C, while MgO needs higher melting temperature.

The phase diagram of the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system is shown in Fig. 3.2. The main phases formed include forsterite, pyroxene, clinopyroxene, cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), sapphire ($\text{Mg}_4\text{Al}_{10}\text{Si}_2\text{O}_{23}$), magnesium oxide, corundum (Al_2O_3), cristobalite (s6) and tridymite (s4), spinel and mullite with the different contents of MgO , Al_2O_3 and SiO_2 . The oxide contents corresponding to various invariant points and the corresponding temperatures in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system are shown in Table 3.1. The melting points of eutectics formed by different phases vary from 1362 to 1646 °C. Among them, the eutectic formed by cordierite, clinopyroxene and tridymite possesses a minimum melting point of 1362 °C (point 13 in Fig. 3.2) and the corresponding contents of MgO , SiO_2 and Al_2O_3 are 23.86 wt%, 61.50 wt% and 14.64 wt%, respectively, with the MgO/SiO_2 mass ratio of 0.39. Except the melting points of the eutectics (points 11, 12 and 13 in Fig. 3.2) with cordierite participation below 1381 °C, the melting temperature of eutectics formed by other phases in the system is higher than 1414 °C.

The RKEF process can use saprolitic laterite ore as raw material with the alumina content of 2–5 wt%. The alumina also moves toward the slag during smelting. According to the mass ratio of ferronickel to slag of 0.2–0.25, the corresponding

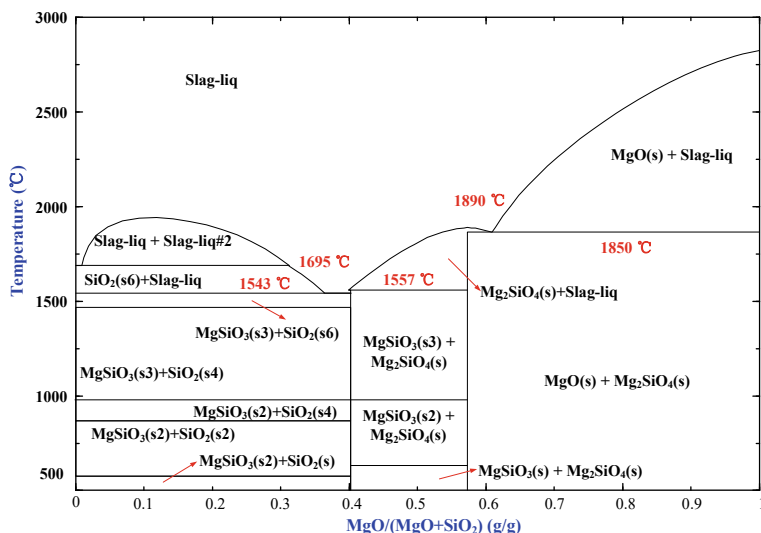


Fig. 3.1 Phase diagram of the $\text{MgO}-\text{SiO}_2$ system

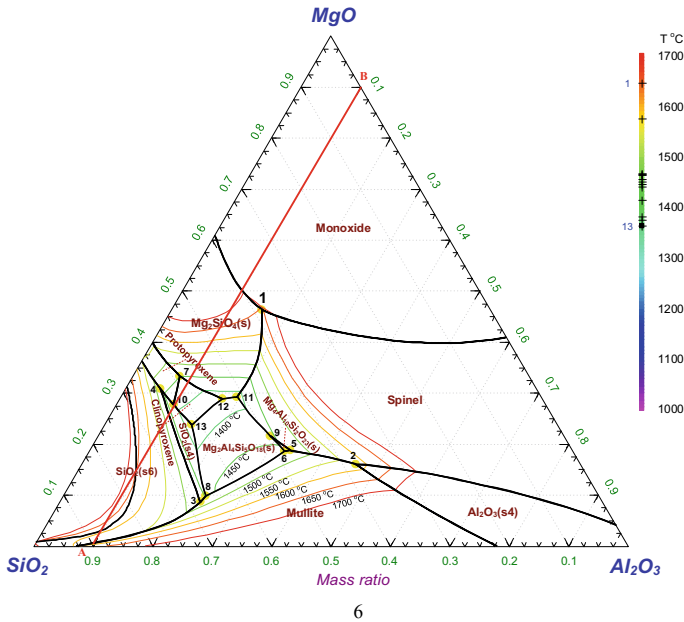


Fig. 3.2 Phase diagram of the MgO–Al₂O₃–SiO₂ system

alumina content in the smelting slag is less than 10 wt%. Hence, cordierite cannot form in an actual slag (line AB in Fig. 3.2). In practice, pyroxene is the main phase in slag with high melting temperature. Considering that the slag has the MgO/SiO₂ mass ratio of 0.6–0.7 and Al₂O₃ content of 3–6 wt%, the main phases will include forsterite (2MgO·SiO₂) and pyroxene (MgO·SiO₂), rendering a liquidus temperature range from 1550 to 1650 °C. It is basically consistent with the smelting temperature of current RKEF process.

The contents of components corresponding to the range of different isotherms are shown in Table 3.2. In the liquid isotherm temperature range 1350–1400 °C, the corresponding contents of MgO, SiO₂ and Al₂O₃ are 18–31 wt%, 50–63 wt% and 11–22 wt%, respectively, in the MgO–Al₂O₃–SiO₂ system. The corresponding MgO/SiO₂ mass ratio is 0.29–0.56. However, the lowest content of Al₂O₃ in this area is 11 wt%, which makes the melting temperature of slag difficult to drop below 1400 °C.

With the increase in the isotherm temperature, the range of MgO, SiO₂ and Al₂O₃ contents gradually expands. In the isotherms ranges of 1350–1450 °C and 1350–1500 °C, the alumina content increases from 18–31 wt% to 7–32 wt% and 3–38 wt%, respectively, which meets the requirements of the actual slag within the lower limit of alumina content. At this moment, the range of MgO content is 27–35 wt% and the MgO/SiO₂ mass ratio is 0.37–0.67.

Above all, in the electric furnace smelting process, with control of only contents of magnesium oxide, silica and alumina components, the lowest melting temperature

Table 3.1 Oxides contents of invariant points and corresponding melting points in the MgO–Al₂O₃–SiO₂ system

No.	Content (wt%)			Main phases	Melting point (°C)
	MgO	SiO ₂	Al ₂ O ₃		
1	46.39	38.41	15.20	Forsterite, monoxide, and spinel	1646
2	16.11	37.82	46.07	Corundum, mullite, and spinel	1575
3	8.66	67.67	23.67	Mullite, cristobalite, and tridymite	1465
4	30.82	63.28	5.90	Pyroxene, cristobalite, and tridymite	1465
5	18.74	47.44	33.82	Sapphire, mullite, and spinel	1464
6	18.71	48.45	32.84	Cordierite, sapphire, and mullite	1455
7	33.34	58.76	7.90	Clinopyroxene, forsterite, and pyroxene	1449
8	9.89	66.10	24.01	Cordierite, mullite, and tridymite	1445
9	21.58	49.43	28.99	Cordierite, sapphire, and spinel	1440
10	27.77	62.63	9.60	Clinopyroxene, pyroxene, and tridymite	1414
11	29.25	51.22	19.53	Cordierite, forsterite, and spinel	1381
12	28.94	53.78	17.28	Clinopyroxene, cordierite, and forsterite	1374
13	23.86	61.50	14.64	Clinopyroxene, cordierite, and tridymite	1362

Table 3.2 Oxides contents in different isotherm regions in the MgO–Al₂O₃–SiO₂ system

Isotherm region (°C)	Content (wt%)			MgO/SiO ₂ mass ratio
	MgO	SiO ₂	Al ₂ O ₃	
1350–1400	18–31	50–63	11–22	0.29–0.56
1350–1450	10–33	47–67	7–32	0.15–0.70
1350–1500	7–37	44–72	3–38	0.08–0.81
1350–1550	3–39	40–79	0–43	0.04–0.88
1350–1600	0–42	36–93	0–48	0–1.02

of slag would be higher than 1400 °C, even close to 1450 °C. It will have the negative impact on the formation of liquid phase in the smelting process.

3.1.2 *MgO–SiO₂–Al₂O₃–FeO Slag System*

Due to the addition of coke, the smelting process of laterite ore is always carried out in a strong reducing atmosphere. The ferric oxide follows the stepwise reduction reactions $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. Therefore, the slag always contain certain amounts of ferrous oxide during smelting. In addition, for improving the Ni grade in ferronickel, the slag is also left with a certain amount of FeO. Considering that the slag with a high SiO₂ content is a typical acidic slag, FeO will act as the basic reactant. The phase diagram of the MgO–SiO₂–FeO system is shown in Fig. 3.3 and the oxides contents of various invariant points and the corresponding temperatures are shown in Table 3.3.

As shown in Fig. 3.3, with the change of the contents of oxides, the main phases are olivine (2MgO·2FeO·SiO₂), clinopyroxene, pyroxene, cristobalite, tridymite and magnesium oxide in the MgO–SiO₂–FeO system. The melting point of the eutectic formed by olivine is low, as shown in Table 3.3. The melting point of the eutectic formed by olivine, clinopyroxene and pyroxene is the minimum of 1295 °C (point 4 in Fig. 3.3). The corresponding contents of MgO, SiO₂ and FeO are 7.74 wt%, 43.82 wt% and 48.44 wt%, respectively, with the MgO/SiO₂ mass ratio of 0.64.

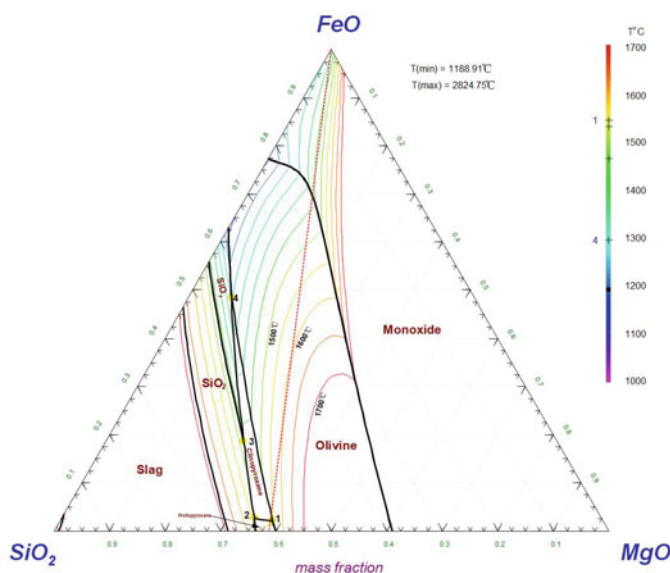


Fig. 3.3 Phase diagram of the MgO–SiO₂–FeO system

Table 3.3 Oxides contents of invariant points and corresponding melting points in the MgO–SiO₂–FeO system

No.	Contents (wt%)			Main phases	Melting point (°C)
	FeO	SiO ₂	MgO		
1	2.04	59.58	38.38	Olivine, pyroxene, and clinopyroxene	1546
2	2.71	62.61	34.69	Pyroxene, clinopyroxene, and cristobalite	1533
3	18.60	56.52	24.88	Clinopyroxene, cristobalite, and tridymite	1465
4	48.44	43.82	7.74	Olivine, clinopyroxene, and tridymite	1295

Figure 3.4 shows the phase diagram of the MgO–Al₂O₃–SiO₂–10 wt% FeO system. Compared with the MgO–Al₂O₃–SiO₂ system (Fig. 3.2), the original forsterite is transformed into olivine in the presence of FeO, due to the combination of forsterite with FeO. In addition, the sapphire disappears in the MgO–SiO₂–Al₂O₃–10 wt% FeO slag system. The other phases have little change and the existence area and melting point of each phase are different.

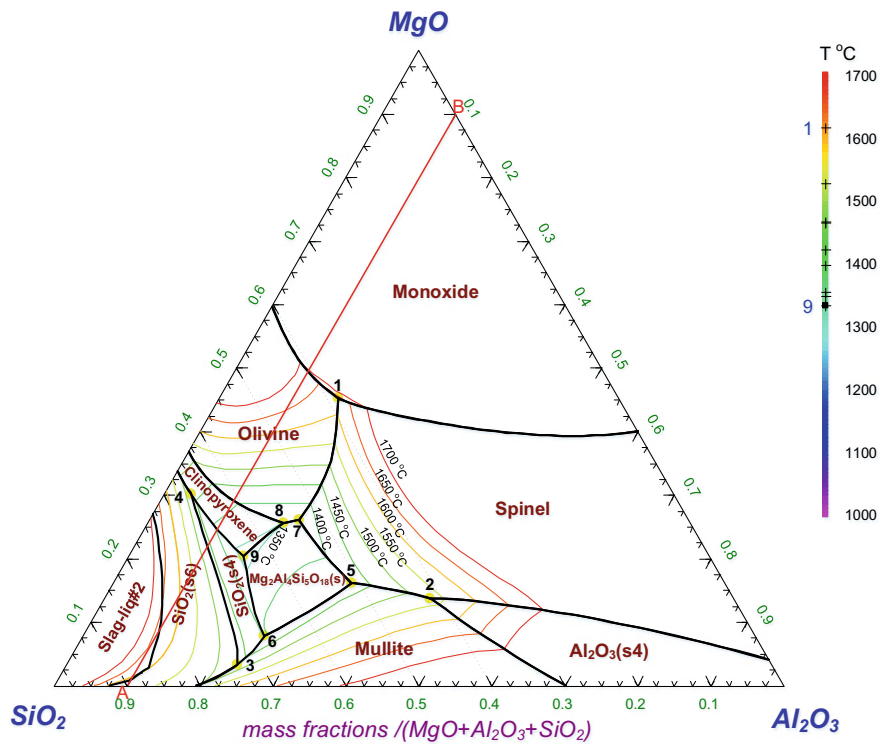


Fig. 3.4 Phase diagram of the MgO–Al₂O₃–SiO₂–10 wt% FeO system [FeO/(MgO + Al₂O₃ + SiO₂) = 10 wt%]

As shown in Table 3.4, the lowest melting point phase is still cordierite in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-10 wt\% FeO}$ slag system and the lowest melting point of eutectic is formed by cordierite, clinopyroxene and tridymite. The melting point decreases from 1362 °C (Table 3.2) in the absence of FeO to 1334 °C in the presence of 10 wt% FeO. Besides, by comparing the temperature isotherms in Figs. 3.2 and 3.4, it can be found that the lowest isotherm temperature of $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ slag system decreases from 1400 to 1350 °C when it contains 10 wt% FeO. From Table 3.4, when forsterite is transformed into olivine, the melting point of the eutectic formed by cordierite, olivine and spinel is 1354 °C. The melting point of the eutectic formed by clinopyroxene, cordierite and olivine is 1349 °C, with decreases of 27 °C and 25 °C, respectively, compared with the eutectic formed in the absence of FeO. These results confirm that the existence of ferrous oxide is beneficial to reduction of the melting temperature of slag.

As shown in Table 3.5, when the melting temperature is below 1350 °C, the contents of MgO, SiO_2 and Al_2O_3 are 16.2–23.4 wt%, 49.5–58.5 wt% and 12.6–17.1 wt%, respectively, with the MgO/ SiO_2 mass ratio of 0.28–0.47. The content of Al_2O_3 in smelting slag is generally below 10 wt%, which is lower than the minimum Al_2O_3 content in the isotherm region of 1350 °C. According to Fig. 3.4, cordierite cannot form under this condition. Therefore, the melting temperature of actual slag will be higher than 1350 °C and the melting temperature of slag increases with the decrease of Al_2O_3 content. When the content of Al_2O_3 is 0.9–8.1 wt%, the melting temperature of slag maintains in the range 1400–1500 °C by controlling the MgO/ SiO_2 mass ratio, as shown in Table 3.5.

Table 3.4 Oxides contents of invariant points and the corresponding melting points in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-10 wt\% FeO}$ system

No.	Content (wt%)			Main phases	Melting point (°C)
	MgO	SiO_2	Al_2O_3		
1	45.29	38.49	16.22	Olivine, monoxide, and spinel	1617
2	13.81	41.54	44.64	Corundum, mullite, and spinel	1528
3	3.35	73.21	23.44	Mullite, cristobalite, and tridymite	1465
4	30.28	66.14	3.58	Clinopyroxene, cristobalite, and tridymite	1465
5	16.18	51.17	32.64	Cordierite, mullite, and spinel	1421
6	7.86	67.31	24.83	Cordierite, mullite, and tridymite	1398
7	26.09	53.42	20.49	Cordierite, olivine, and spinel	1354
8	25.69	55.77	18.54	Cordierite, clinopyroxene, and olivine	1349
9	20.39	63.89	15.72	Cordierite, clinopyroxene, and tridymite	1334

Table 3.5 Oxides contents in different isotherm regions in the MgO–Al₂O₃–SiO₂–10 wt% FeO system

Isotherm region (°C)	Content (wt%)			MgO/SiO ₂ mass ratio
	MgO	SiO ₂	Al ₂ O ₃	
1300–1350	16.2–23.4	49.5–58.5	12.6–17.1	0.28–0.47
1300–1400	6.7–26.1	45–60.7	8.1–24.3	0.11–0.57
1300–1450	4.5–28.8	42.7–64.8	4.5–32.4	0.07–0.67
1300–1500	0.9–32.4	39.6–71.1	0.9–37.8	0.01–0.78
1300–1550	0–34.2	36–77.4	0–42.3	0–0.85
1300–1600	0–38.7	32.4–85.5	0–46.8	0–1.08

In the actual smelting process, the MgO/SiO₂ mass ratio is generally controlled by the mixing various laterite ores with different compositions in the absence of fluxes. The MgO/SiO₂ mass ratio is controlled at 0.5–0.7 and the optimal range is 0.60–0.65. In addition, the content of ferrous oxide in the slag is generally controlled at 5–10 wt%. According to Fig. 3.4, the slag is dominated by forsterite and the melting temperature is 1420–1550 °C under this condition. The melting temperature increases with the decrease of Al₂O₃ content and the increase of MgO/SiO₂ mass ratio.

In the actual process, both the melting temperature of slag and the fluidity of molten iron should be considered. In order to ensure slag properties and separation of molten iron from slag, the smelting temperature should be at least 1500–1550 °C. Under this condition, when the MgO/SiO₂ mass ratio is 0.5–0.7, the range of Al₂O₃ content can be expanded to 0–10 wt%.

The phase diagrams of the MgO–Al₂O₃–SiO₂–FeO slag system with FeO content of 20 wt% and 30 wt% are shown in Figs. 3.5 and 3.6, respectively. The results indicate that the change of FeO content has weak effects on the phase composition but exerts a great effect on the melting temperature of the slag. The lowest melting temperature decreases from 1334 to 1302 °C with the increase of the FeO content from 10 to 20 wt%. When the content of FeO reaches 30 wt%, the lowest melting temperature of slag further decreases to 1273 °C, which is about 61 °C lower than that of FeO at 10 wt%.

It should be noted that about 60–70 wt% of iron in laterite ore is enriched in the ferronickel alloy after smelting and the final slag has a relatively low ferrous oxide content. Hence, the phase diagrams shown in Figs. 3.5 and 3.6 provide only the qualitative analyses. The above analyses clarify that the reduction degree of iron oxides in laterite ore in rotary kiln would have the great influence on the melting performance of reduction product (calcine from rotary kiln) in the electric furnace smelting. Hence, by strengthening the selective reduction of iron oxide in the rotary kiln, the melting temperature of calcine in the electric furnace can be reduced due to the increase of FeO content, contributing to smelting with high melting speed and low electricity consumption.

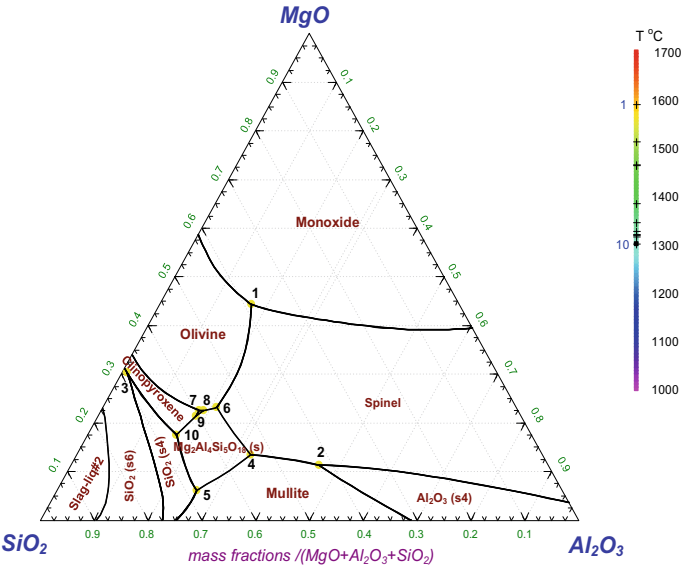


Fig. 3.5 Phase diagram of the MgO–Al₂O₃–SiO₂–20 wt% FeO system [FeO/(MgO + Al₂O₃ + SiO₂) = 20 wt%]

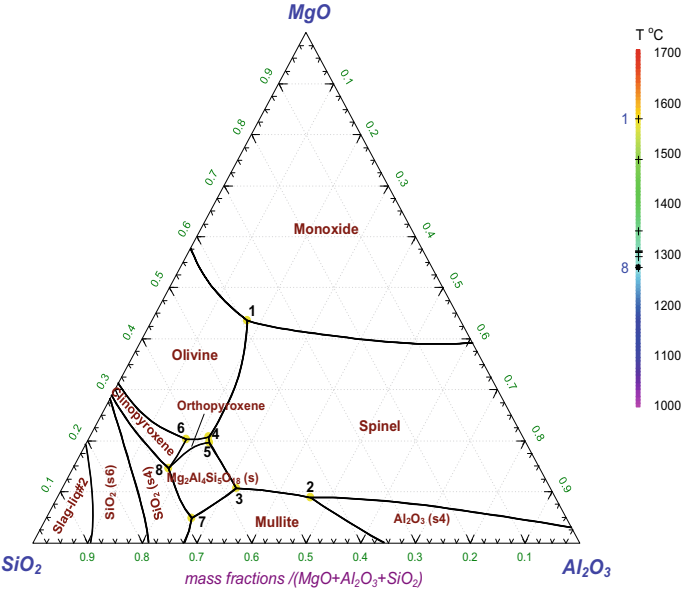


Fig. 3.6 Phase diagram of the MgO–Al₂O₃–SiO₂–30 wt% FeO system [FeO/(MgO + Al₂O₃ + SiO₂) = 30 wt%]

3.1.3 $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$ Slag System

Due to the high temperature of liquid phase formation in laterite ore, the fluxes, such as quick lime and limestone, are usually added to reduce the melting temperature of feeds during smelting. The phase diagram of the CaO-MgO-SiO_2 system is shown in Fig. 3.7 and the component contents of invariant points are shown in Table 3.6.

By comparing Fig. 3.2 with Fig. 3.7, the main phases in the CaO-MgO-SiO_2 system are obviously different from those in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system. Because the binding ability of CaO and SiO_2 is stronger than that of MgO and SiO_2 , the lowest point of eutectic in the CaO-MgO-SiO_2 system decreases significantly. All kinds of pyroxenes in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system are transformed into calcium silicate. With the increase of CaO content in the system, calcium silicate is transformed into wollastonite (CaSiO_3), $\alpha\text{-Ca}_2\text{SiO}_4$, and rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$). The lowest melting phase of the system transforms from cordierite to diopside ($\text{CaMgSi}_2\text{O}_6$). The lowest point eutectic is formed by the diopside, wollastonite and tridymite. The corresponding contents of CaO , MgO and SiO_2 are 30.09 wt%, 9.13 wt% and 60.78 wt%, respectively. Compared with the lowest melting point of 1362 °C in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system, the one for the CaO-MgO-SiO_2 system is 1327 °C, decreased by 35 °C. However, with the same MgO/SiO_2 mass ratio of slag, as the CaO content increases, diopside is gradually transformed into akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$), lowering the melting temperature of slag.

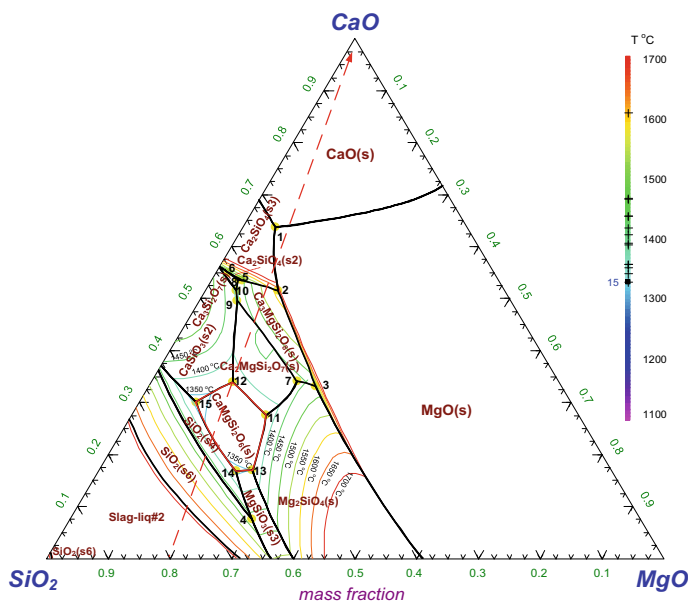


Fig. 3.7 Phase diagram of the CaO-MgO-SiO_2 system

Table 3.6 Oxides contents of invariant points and the corresponding melting points in the CaO–MgO–SiO₂ system

No.	Content (wt%)			Main phases	Melting point (°C)
	CaO	SiO ₂	MgO		
1	63.75	31.05	5.21	α -Ca ₂ SiO ₄ , periclase, and CaO	1877
2	51.52	36.70	11.78	α -Ca ₂ SiO ₄ , merwinite, and CaO	1609
3	33.15	39.81	27.04	Merwinite, forsterite, and CaO	1467
4	7.50	62.99	29.51	Enstatite, cristobalite, and tridymite	1465
5	53.52	41.58	4.90	α -Ca ₂ SiO ₄ , γ -Ca ₂ SiO ₄ , and merwinite	1437
6	54.91	43.01	2.07	γ -Ca ₂ SiO ₄ , merwinite, and rankinite	1437
7	34.06	42.42	23.53	Akermanite, merwinite, and forsterite	1418
8	53.61	42.15	4.25	γ -Ca ₂ SiO ₄ , merwinite, and rankinite	1406
9	49.58	44.28	6.14	Akermanite, merwinite, and wollastonite	1392
10	51.57	43.51	4.92	Merwinite, rankinite, and wollastonite	1389
11	27.58	50.66	21.76	Akermanite, diopside, and forsterite	1358
12	33.93	52.87	13.20	Akermanite, diopside, and wollastonite	1357
13	16.97	58.17	24.86	Diopside, forsterite, and enstatite	1351
14	16.81	60.93	22.26	Diopside, enstatite, and tridymite	1341
15	30.09	60.78	9.13	Diopside, wollastonite, and tridymite	1327

The oxides contents in different isotherms of the CaO–MgO–SiO₂ system are shown in Table 3.7. Compared with the MgO–Al₂O₃–SiO₂ system in Table 3.1, an isotherm range of 1300–1350 °C appears in CaO–MgO–SiO₂ slag system, which indicates that the melting temperature of slag can be reduced with a specified CaO content. The content ranges of CaO, MgO and SiO₂ are (16–19)/(27–32) wt%, (7.5–11.5)/(20–24) wt%, and 57.5–62 wt% with the MgO/SiO₂ mass ratios of 0.12–0.21 and 0.32–0.42, respectively. It should be noted that the MgO/SiO₂ mass ratio is relatively low under this condition and it is difficult to realize in the actual laterite ore.

Table 3.7 Oxides contents in different isotherm regions in the CaO–MgO–SiO₂ system

Isotherm region (°C)	Content (wt%)			MgO/SiO ₂ mass ratio
	CaO	MgO	SiO ₂	
1300–1350	16–19, 27–32	7.5–11.5, 20–24	57.5–62	0.12–0.21, 0.32–0.42
1300–1400	13–40	3–27.5	47.5–63	0.05–0.48
1300–1450	8–56	0–31	41–64	0–0.61
1300–1500	4.5–56	0–35	40–66	0–0.72
1300–1550	0–56.5	0–38.5	40.2–67.5	0–0.80
1300–1600	0–57	0–61.5	41–70	0–0.89

By comparing Table 3.1 with Table 3.7, within the same isotherm region, the range of the MgO/SiO₂ mass ratio increases with the addition of CaO. For example, the MgO/SiO₂ mass ratio in the CaO–MgO–SiO₂ system increases to 0.05–0.48, and that in the MgO–Al₂O₃–SiO₂ slag system varies from 0.29 to 0.56 in the isotherm below 1400 °C. It shows that the addition of CaO affects the content range of other oxides, which controls the melting temperature of slag.

The phase diagrams of the CaO–MgO–SiO₂–Al₂O₃ system with Al₂O₃ contents of 5 wt% and 10 wt% are shown in Figs. 3.8 and 3.9, respectively. Compared with the phase diagram of the CaO–MgO–SiO₂ system, the phase compositions of the CaO–MgO–SiO₂–Al₂O₃ system with Al₂O₃ contents of 5 and 10 wt% have no obvious difference. However, the lowest point of eutectic decreases from 1327 to 1279 °C with the increase of Al₂O₃ content from 0 to 5 wt%. With the further increase of Al₂O₃ content to 10 wt%, the lowest melting point further decreases to 1220 °C, decreased by more than 200 °C. These results confirm that the melting temperature of the slag can be reduced by increasing Al₂O₃ content.

Although increasing Al₂O₃ content can reduce the melting temperature of the slag, it can be found from Figs. 3.7, 3.8 and 3.9 that the eutectic with the lowest melting point in the CaO–MgO–SiO₂–Al₂O₃ system is always formed by diopside, wollastonite and tridymite. When the Al₂O₃ content is lower than 10 wt%, the low melting point phase is diopside, which can reduce the formation temperature of liquid phase in slag with the appropriate CaO content.

The oxides contents in different isotherms of the CaO–MgO–SiO₂–5 wt% Al₂O₃ and CaO–MgO–SiO₂–10 wt% Al₂O₃ systems are shown in Tables 3.8 and 3.9,

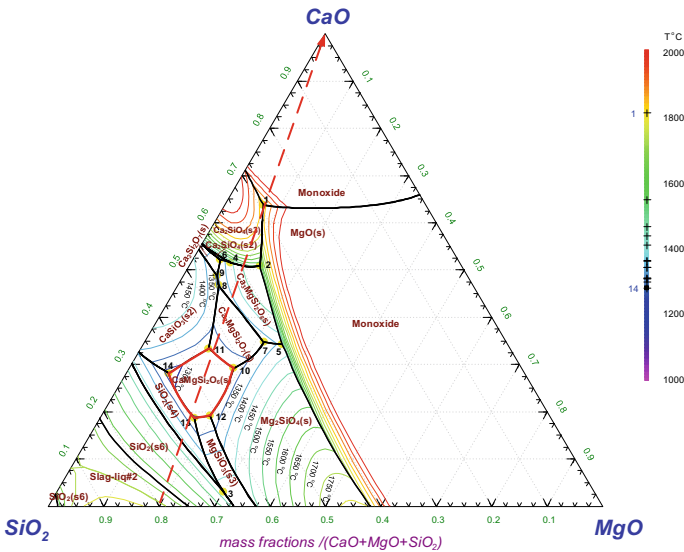


Fig. 3.8 Phase diagram of the CaO–MgO–SiO₂–5 wt% Al₂O₃ system [(Al₂O₃/(CaO + MgO + SiO₂) = 5 wt%]

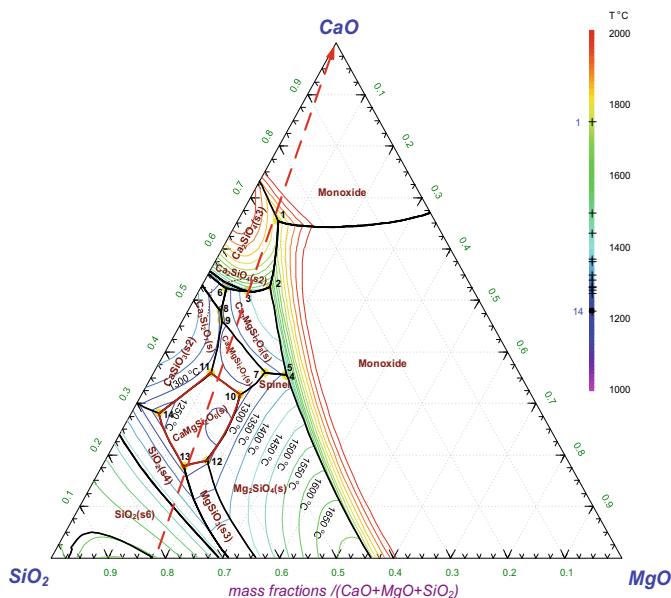


Fig. 3.9 Phase diagram of the CaO–MgO–SiO₂–10 wt% Al₂O₃ system [(Al₂O₃/(CaO + MgO + SiO₂) = 10 wt%]

respectively. Compared with Table 3.7, the lowest isotherm decreases from 1350 °C to 1300 °C and 1250 °C, respectively, when the contents of Al₂O₃ are 5 wt% and 10 wt%. The content of MgO in the lowest isothermal region is in the ranges 6.7–8.6 wt% and 2.7–6.8 wt%, respectively, which are lower than the MgO content in the actual smelting slag. Under these conditions, the MgO/SiO₂ mass ratio is relatively low, which is difficult to realize in the actual smelting slag. Hence, it is necessary to consider the isotherm range at higher temperature and the corresponding oxides contents. According to Fig. 3.8 and Table 3.8, when the Al₂O₃ content reaches 5 wt%, the contents of CaO and MgO increase, respectively, to 14.2–36.6 wt% and 8.6–20.9 wt% with the MgO/SiO₂ mass ratio of 0.17–0.44, which can reduce the melting temperature to 1300–1350 °C. Compared with the slag in the absence of Al₂O₃, the melting temperature decreases by about 50 °C. As the Al₂O₃ content increases to 10 wt%, the melting temperature of slag is further reduced to 1250–1300 °C by controlling the contents of CaO and MgO to 14.4–44.1 wt% and 6.8–17.1 wt%, respectively, with the MgO/SiO₂ mass ratio of 0.11–0.39.

Considering the existence of ferrous oxide in the smelting slag, the CaO–MgO–SiO₂–Al₂O₃–FeO phase diagram can be calculated. As shown in Fig. 3.10, the main phase in the CaO–MgO–SiO₂–Al₂O₃–FeO system is similar to that in the CaO–MgO–SiO₂–Al₂O₃ (Al₂O₃ < 10 wt%) system. The lowest melting point phase is still diopside. However, when FeO is present, the lowest eutectic point in the slag system is only 1185 °C. Compared with the CaO–MgO–SiO₂–5 wt% Al₂O₃ and CaO–MgO–SiO₂–10 wt% Al₂O₃ systems, the lowest melting temperature is decreased

Table 3.8 Content ranges of the components in different isotherm regions in the CaO–MgO–SiO₂–5 wt% Al₂O₃ system

Isotherm region (°C)	Content (wt%)				MgO/SiO ₂ mass ratio
	CaO	MgO	SiO ₂	Al ₂ O ₃	
1250–1300	23.8–28.5	6.7–8.6	58–61.8	4.8	0.11–0.17
1250–1350	14.2–36.6	2.9–20.9	45.6–63.6	4.8	0.05–0.44
1250–1400	10.5–51.3	0–24.7	39.9–64.6	4.8	0–0.57
1250–1450	5.7–52.3	0–29.5	39.0–66.5	4.8	0–0.67
1250–1500	0–52.3	0–36.1	39.9–68.4	4.8	0–0.71
1250–1550	0–53.2	0–38.0	39.9–70.3	4.8	0–0.79
1250–1600	0–53.2	0–39.9	40.9–73.2	4.8	0–0.84

Table 3.9 Content ranges of the components in different isotherm regions in the CaO–MgO–SiO₂–10 wt% Al₂O₃ system

Isotherm region (°C)	Content (wt%)				MgO/SiO ₂ mass ratio
	CaO	MgO	SiO ₂	Al ₂ O ₃	
1200–1250	22.5–27.9	2.7–6.8	56.7–61.2	9.1	0.05–0.11
1200–1300	14.4–44.1	0.9–17.1	41.4–63	9.1	0.01–0.39
1200–1350	8.1–49.5	0–20.3	37.8–64.8	9.1	0–0.54
1200–1400	4.5–49.9	0–24.8	36–66.2	9.1	0–0.61
1200–1450	0–50	0–33.3	35.1–67.9	9.1	0–0.67
1200–1500	0–50.1	0–35.1	31.5–70.2	9.1	0–0.74
1200–1550	0–50.1	0–37.8	31.5–73.4	9.1	0–0.82
1200–1600	0–50.1	0–39.6	31.5–76.5	9.1	0–0.90

by 94 °C and 35 °C, respectively, in the presence of 10 wt% FeO. These results confirm that the melting property of slag is improved with the addition of FeO in the CaO–MgO–SiO₂–Al₂O₃ slag system.

As shown in Table 3.10, the region of diopside formation in the slag system is basically included in the isotherm of 1250 °C, indicating that the addition of FeO is favorable to reduction of the melting temperature of diopside phase. Compared with CaO–MgO–SiO₂–Al₂O₃ slag system, the isotherm range of 1250 °C in the CaO–MgO–SiO₂–Al₂O₃–FeO system increases obviously. Although there is an isotherm region of 1200 °C in the slag system, the content of MgO in laterite ore is difficult to reach the required range. In the 1250 °C isotherm, there are some areas with high content of MgO, which can meet the actual content of MgO in laterite ore. It means that the melting temperature of slag can be reduced to about 1250 °C in the smelting process by regulating contents of other oxides.

According to the above phase diagrams, it can be found that the MgO, SiO₂ and Al₂O₃ in laterite ore have significant influence on the phase formation and the melting properties of slag during smelting. Generally, pyroxene

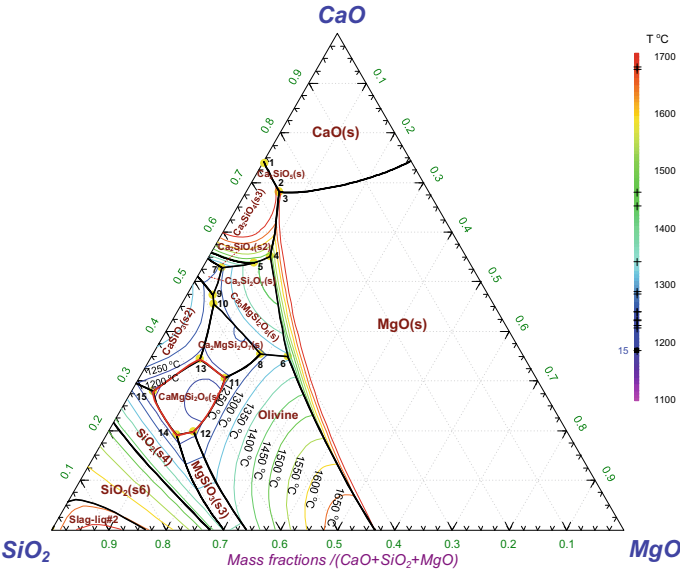


Fig. 3.10 Phase diagram of the CaO–MgO–SiO₂–8 wt% Al₂O₃–10 wt% FeO system [(Al₂O₃/(CaO + MgO + SiO₂) = 8 wt%; (FeO/(CaO + MgO + SiO₂) = 10 wt%]

Table 3.10 Content ranges of components in different isotherm regions in the CaO–MgO–SiO₂–8 wt% Al₂O₃–10 wt% FeO system

Isotherm region (°C)	Content (wt%)				MgO/SiO ₂ mass ratio
	CaO	MgO	SiO ₂	Al ₂ O ₃	
1150–1200	22.9–25.0	2.5–4.2	56.4–58.5	6.8	0.04–0.08
1150–1250	14.8–31.3	0–13.6	45.3–60.2	6.8	0–0.29
1150–1300	11.0–44.9	0–16.9	36.9–61.4	6.8	0–0.45
1150–1350	6.8–46.6	0–20.3	35.6–62.3	6.8	0–0.59
1150–1400	0–47.0	0–27.5	33.9–64.4	6.8	0–0.64
1150–1450	0–47.5	0–30.9	31.4–66.1	6.8	0–0.72
1150–1500	0–47.9	0–33.1	28.8–67.8	6.8	0–0.79
1150–1550	0–48.3	0–35.6	27.6–70.3	6.8	0–0.88
1150–1600	0–49.2	0–37.7	26.7–74.1	6.8	0–1.0

is the main phase with high melting temperature (melting point > 1550 °C), which is unfavorable to the formation of liquid phase. With the increase of CaO content, the low melting point phase of slag changes and diopside is formed in the proper range of oxides, leading to the obvious decrease of melting temperature. In addition, increasing content of Al₂O₃ is also beneficial to the decrease of the melting temperature of slag. Therefore, the basicity of slag can be expressed by quaternary

Table 3.11 Contents of various components for the lowest liquidus temperature ranges in different slag systems

Slag system	Lowest liquidus temperature (°C)	MgO/SiO ₂ mass ratio	R ₄
MgO–Al ₂ O ₃ –SiO ₂ (Al ₂ O ₃ < 10 wt%)	1400–1450	0.41–0.60	0.37–0.49
CaO–MgO–SiO ₂ –0 wt% Al ₂ O ₃	1350–1400	0.21–0.48	0.59–1.11
CaO–MgO–SiO ₂ –5 wt% Al ₂ O ₃	1300–1350	0.17–0.44	0.46–0.98
CaO–MgO–SiO ₂ –10 wt% Al ₂ O ₃	1250–1300	0.11–0.39	0.38–0.96
MgO–Al ₂ O ₃ –SiO ₂ –10 wt% FeO (Al ₂ O ₃ < 10 wt%)	1350–1400	0.48–0.59	0.33–0.37
CaO–MgO–SiO ₂ –8 wt%Al ₂ O ₃ –10 wt% FeO	1200–1250	0–0.29	0.37–0.76

basicity [$R_4 = m(\text{CaO} + \text{MgO})/m(\text{SiO}_2 + \text{Al}_2\text{O}_3)$], instead of binary basicity [$R_2 = m(\text{CaO})/m(\text{SiO}_2)$]. Generally, the existence of FeO can exert the favorable effect on the melting properties of slag in the smelting process.

According to the phase diagrams shown in Figs. 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9 and 3.10, and referring to the oxides contents in typical laterite ore, the lowest melting temperature range and the corresponding oxides contents and quaternary basicity can be obtained. As shown in Table 3.11, the lowest melting temperature of the MgO–Al₂O₃–SiO₂ (Al₂O₃ < 10 wt%) system is 1400–1450 °C in the absence of CaO. At this time, it is necessary to control the MgO/SiO₂ mass ratio at 0.41–0.60 and the quaternary basicity at 0.37–0.49 as well as the Al₂O₃ content at 8–10 wt%. When the content of Al₂O₃ is less than 5 wt%, the lowest melting temperature in the MgO–Al₂O₃–SiO₂ system rises to 1450–1500 °C.

In the presence of CaO, the lowest melting temperature in the CaO–MgO–SiO₂–Al₂O₃ system decreases. With the increase of the Al₂O₃ content, the lowest melting temperature tends to decrease more obviously. The lowest melting temperature is 1350–1400 °C in the absence of Al₂O₃. In this case, the quaternary basicity is in the range 0.59–1.11. When the Al₂O₃ content increases to 5 wt% and 10 wt%, respectively, the lowest melting temperature is reduced to 1300–1350 °C and 1250–1300 °C, respectively. Under these conditions, the MgO/SiO₂ mass ratio and quaternary basicity of slag have fluctuations. Except for the increase of the CaO content, the upper and lower limits of the MgO/SiO₂ mass ratio and quaternary basicity moved down.

As shown in Table 3.11, the slag in the presence of FeO can also reduce the low melting temperature zone. Compared with the MgO–Al₂O₃–SiO₂ (5 wt% < Al₂O₃ < 10 wt%) system, the lowest melting temperature of slag decreases from 1400–1450 °C to 1350–1400 °C when the FeO content is from 0 to 10 wt%. In the CaO–MgO–SiO₂–8 wt% Al₂O₃–10 wt% FeO system, the lowest melting temperature reaches the minimum value of 1200–1250 °C. Besides, the MgO/SiO₂ mass ratio and quaternary basicity are 0–0.29 and 0.37–0.76, respectively.

In the ranges of CaO content, MgO content, MgO/SiO₂ mass ratio and quaternary basicity shown in Table 3.11, it is difficult to meet all the requirements in a single laterite ore. In the ferronickel production, different types of laterite ore can be used for ore matching according to a certain proportion to adjust oxide contents, especially for the MgO content and MgO/SiO₂ mass ratio. Due to the low content of CaO in laterite ore, it is generally necessary to adjust the composition by adding quick lime or limestone. Although increasing Al₂O₃ content is beneficial to the melting of slag, this oxide will not be added in the ore matching process generally. The Al₂O₃ in slag basically comes from the laterite ore and ash of reducing agent. Generally, the Al₂O₃ content in slag may vary obviously and can be controlled by ore matching.

3.2 Liquid Phase Formation During Smelting

During smelting in the electric furnace, the initial temperature for the formation of liquid phase and the amount of liquid produced at various temperatures strongly affect the melting rate of the feed. The liquid quantity of the slag during smelting can be analyzed using the FactSage software.

Based on the composition of laterite-A (Table 3.12), the contents of oxides in the CaO–MgO–Al₂O₃–SiO₂–FeO slags were determined (assuming that Ca, Mg, Al, and Si oxides remain in the slag). The slags with different compositions were designed and the effects of various oxides on the liquid phase formation were considered.

3.2.1 Effect of CaO Content

The iron oxide in lateirte nickel ore may be oxidized in the form of ferric oxide after roasting in air. It is assumed that Fe₂O₃, SiO₂, MgO, Al₂O₃ and CaO in laterite ore participate in the formation of liquid phase at high temperature. Considering their contents in laterite-A (Table 3.12), the compositions of slags with different CaO contents were designed, as shown in Table 3.13. The variation of liquid phase amount with temperature is shown in Fig. 3.11. Figure 3.12 shows the change of the phases and the corresponding contents at different temperatures.

As shown in Fig. 3.11, the amount of liquid phase increases with temperature in the range 1100–1600 °C. When the CaO content is 2 wt%, there is no liquid phase in the temperature range 1100–1175 °C. The initial temperature for the liquid phase

Table 3.12 Main chemical composition of laterite-A (wt%)

Fe _{total}	Ni	SiO ₂	MgO	Al ₂ O ₃	CaO	LOI*
22.1	1.9	26.5	13.4	4.3	2.0	13.2

* LOI Loss on ignition

Table 3.13 Designed compositions of slags with various CaO contents (air)

CaO content in the mixture (wt%)	Composition of slag (wt%)				
	Fe ₂ O ₃	CaO	SiO ₂	MgO	Al ₂ O ₃
2.0	40.6	2.6	34.1	17.2	5.5
5.0	39.0	6.4	32.7	16.6	5.3
10.0	36.4	12.7	30.5	15.4	5.0
15.0	33.8	18.9	28.4	14.3	4.6
20.0	31.1	25.4	26.1	13.2	4.2
23.0	29.4	29.4	24.7	12.5	4.0
26.0	27.6	33.7	23.2	11.7	3.8
30.0	25.1	39.7	21.1	10.7	3.4

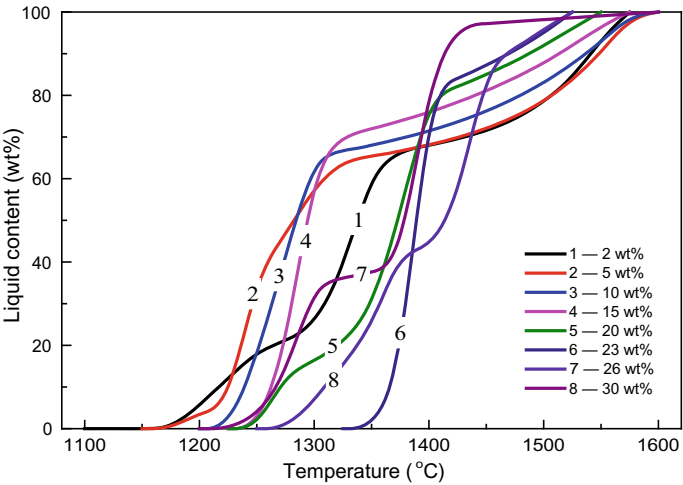


Fig. 3.11 Effect of CaO content on the liquid phase amount with increasing temperature (air)

formation is 1200 °C for laterite ore with 2 wt% CaO content and about 6 wt% of the components are transformed into liquid phase. With the increase of temperature, the amount of liquid phase increases significantly in the range 1200–1350 °C and the liquid amount reaches 61.8 wt% at 1350 °C. When the temperature is above 1375 °C, the increasing trend of liquid phase formation slows down. The components in the slag are completely transformed into liquid phase at 1575 °C.

As shown in Fig. 3.12a, the main phases of slag are pyroxene, diopside and hematite, in addition to small amounts of anorthite and tridymite at 1100 °C with CaO content of 2 wt%. With the increase of temperature, the reaction between hematite and pyroxene is strengthened to form spinel. The content of hematite decreases and the content of spinel increases and reaches a maximum at 1375 °C. When the temperature increases from 1100 to 1175 °C, the proportion of pyroxene increases while the

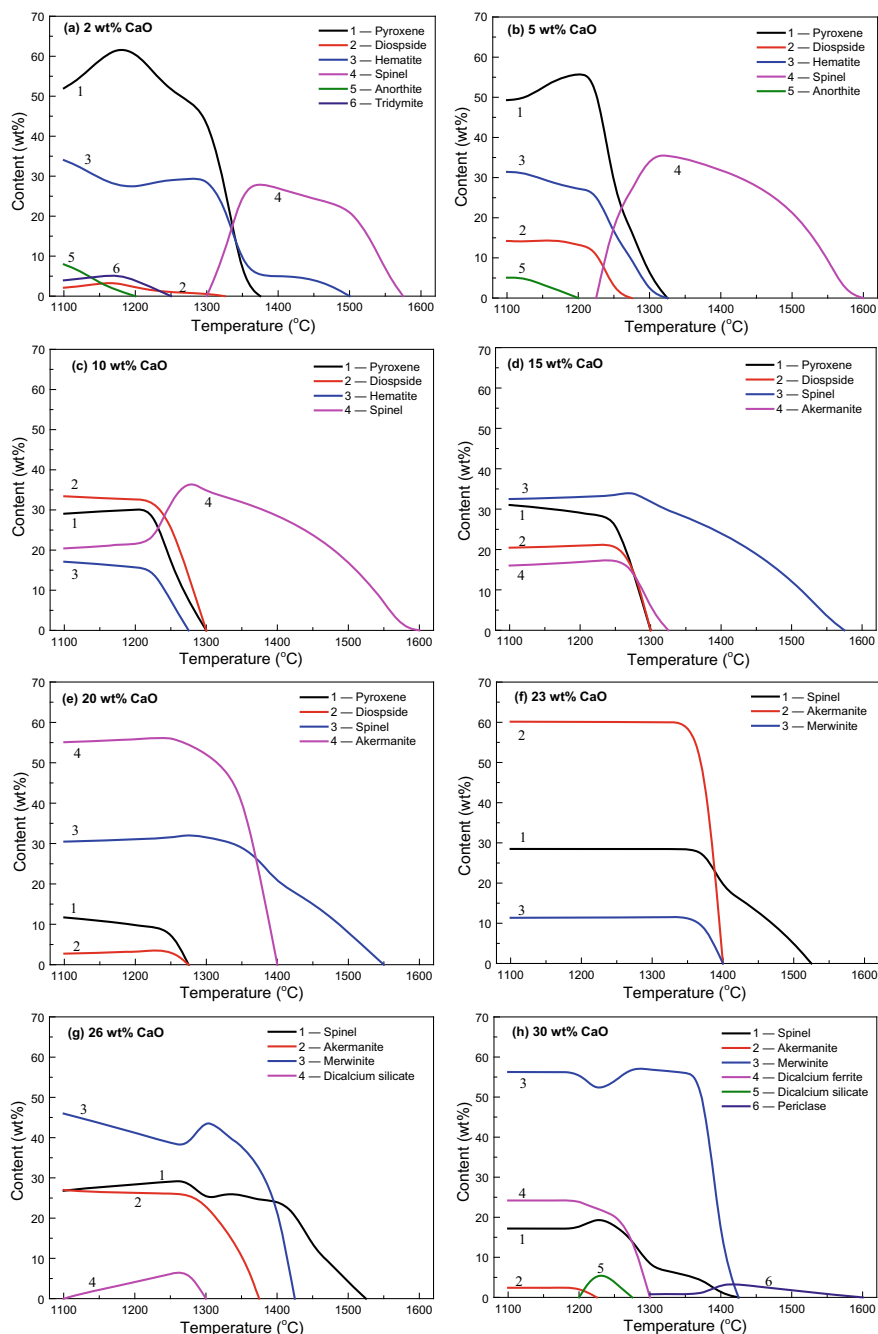


Fig. 3.12 Effect of CaO content on the phase transformation with increasing temperature (air)

proportion of anorthite decreases. At 1200 °C, the low melting point eutectic formed by diopside, anorthite and tridymite begins to melt. Then, the contents of tridymite and pyroxene decrease with increasing temperature and the amount of liquid phase shows an obvious increasing trend. When the temperature exceeds 1375 °C, only spinel and a small amount of hematite exist in the slag. As the temperature further increases, the spinel begins to melt and its content gradually decreases.

With the CaO content of 5 wt%, the initial temperature for the liquid phase formation is still close to 1200 °C. However, when the temperature is higher than 1225 °C, the liquid amount is higher than that when the content of CaO is 2 wt%. Especially, in the temperature range 1250–1375 °C, the amount of liquid phase is significantly higher than that in laterite ore due to the increase of CaO content, which promotes diopside formation (Fig. 3.12b).

With the further increase of CaO content, the initial temperature for the liquid phase formation increases firstly and then decreases. When the CaO content is 10 wt%, the initial temperature for the liquid phase formation is 1250 °C. When the CaO content reaches 15–20 wt%, this temperature increases to 1275 °C. As shown in Fig. 3.12c–e, the diopside still exists when the CaO content is in the range 10–20 wt%. However, the tridymite and anorthite disappear, leading to the increase of the initial temperature for liquid phase formation. This temperature is close to the melting point of diopside. In addition, the amount of diopside is different with different CaO contents, which leads to the difference of the amount of liquid phase at 1250–1300 °C. As the CaO content increases from 2 wt% to 20 wt%, the diopside proportion increases firstly and then decreases. Accordingly, the amount of liquid phase shows the same trend at 1300 °C. For example, when the CaO content is 10 wt%, the maximum amount of diopside is 33.4 wt%. Hence, the liquid phase reaches the maximum of 65.4 wt% at 1300 °C.

When the content of CaO exceeds 23 wt%, the diopside disappears while the akermanite, merwinite and spinel appear (Fig. 3.12f–h). The formation of these phases with high melting point significantly increases the initial melting temperature of slag to more than 1350 °C. However, when the content of CaO is 30 wt%, a large amount of calcium ferrite is formed, which decreases the initial temperature for the liquid phase formation to about 1250 °C.

As shown in Fig. 3.12, there are a large number of spinel phase in the CaO content range 2–30 wt%. Spinel has a higher melting point than other phases, and it can only be transformed into liquid phase at temperature above 1550 °C. It affects the amount of liquid phase at relatively low temperature. In addition, the existence of solid phase in the molten liquid phase will have a negative impact on the fluidity of slag.

In the process of reductive roasting and smelting, the iron oxide in laterite ore is gradually reduced to ferrous oxide and metallic iron with the extension of time. It is assumed that FeO, SiO₂, MgO, Al₂O₃ and CaO participate in the liquid phase formation at high temperature and the FeO content is assumed to be 10 wt%. The designed compositions of slags with various CaO contents are shown in Table 3.14. Compared with the liquid phase formation in air, the initial temperature for the liquid phase formation obviously decreases when the FeO content is 10 wt%. The initial formation temperature of liquid phase is 1200 °C when the CaO

Table 3.14 Designed compositions of slags with various CaO contents (FeO content: 10 wt%)

CaO content in the mixture (wt%)	Composition of slag (wt%)				
	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃
2.0	10.0	3.9	51.6	26.1	8.4
5.0	10.0	9.4	48.3	24.4	7.8
10.0	10.0	17.9	43.2	21.9	7.0
15.0	10.0	25.7	38.5	19.5	6.2
20.0	10.0	33.2	34.1	17.2	5.5
23.0	10.0	37.5	31.4	15.9	5.1
26.0	10.0	41.9	28.9	14.6	4.7
30.0	10.0	47.8	25.3	12.8	4.1

content is 5–15 wt%. Compared with Figs. 3.12 and 3.14, the pyroxene transforms into olivine in the presence of FeO. Particularly, with the CaO content of 20 wt%, the proportion of olivine is more than 80 wt% at 1100–1300 °C (Fig. 3.14e).

With the CaO content of 2 wt%, the initial temperature for the liquid phase formation is 1225 °C, which is slightly higher than the initial temperature for the liquid phase formation in air. By comparing with Figs. 3.12a and 3.14a, diopside and anorthite form a solid solution in the presence of ferrous oxide. The melting point of this solid solution is higher than that of solid solution formed by diopside, anorthite and tridymite, which leads to the increase of initial melting temperature.

When the CaO content is 5–15 wt%, the initial temperature for the liquid phase formation decreases to 1200 °C. Compared with the case containing 2 wt% CaO, the liquid amount with the CaO content of 5–15 wt% increases in the temperature range 1200–1350 °C. For example, the amount of liquid phase reaches 63 wt% and 68 wt% with the CaO content of 5 wt% and 10 wt%, respectively, when temperature is 1250 °C. However, the liquid amount is only 33 wt% with CaO content of 2 wt% (Fig. 3.13). By comparing Fig. 3.14a with Fig. 3.14d, the main reason for the difference in the liquid production caused by varying CaO content is associated with the formation of diopside. When the CaO content is 5 wt% and 10 wt%, the maximum amount of diopside is 18 wt% and 25 wt%, respectively. As a result, the liquid phase amount reaches the maximum in the temperature range 1200–1340 °C.

When the CaO content is above 20 wt%, the initial temperature for the liquid phase formation increases obviously. With the CaO content of 20–23 wt%, the initial temperature for the liquid phase formation maintains at 1275–1300 °C. However, at the same temperature, the liquid amounts of slags with low CaO contents are always higher than those of slags with high CaO contents. The difference of liquid amount is attributed to the difference of olivine formation. With the CaO content of 20 wt%, the olivine content reaches the maximum value of about 84 wt% and then the olivine content decreases with increasing CaO content. When the CaO content is 23 wt%, the content of olivine decreases to 41 wt%. There are different amounts of liquid phase formed by melting of olivine in the temperature range 1300–1400 °C.

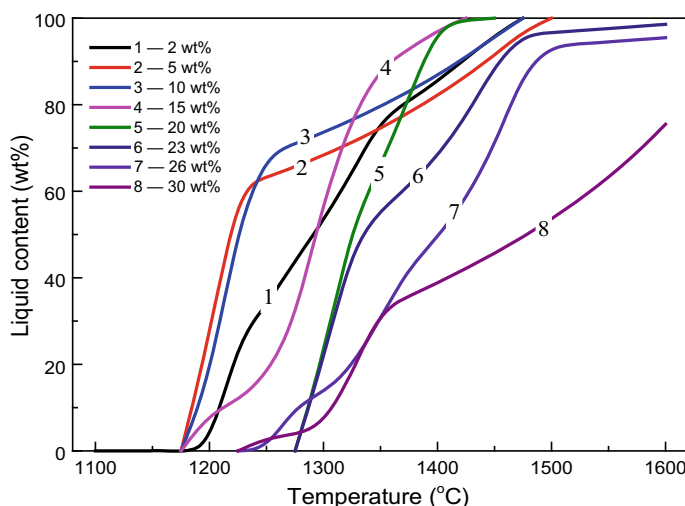


Fig. 3.13 Effect of CaO content on the liquid phase amount with increasing temperature by fixing FeO content of 10 wt%

When the CaO content increases to 26 wt%, the olivine disappears and the main phases consist of merwinite, spinel, dicalcium silicate and periclase. The initial temperature for the liquid phase formation decreases to 1250 °C. However, the amount of liquid phase is as low as 0.3 wt% and 3 wt%, respectively, at this temperature, mainly due to the melting of dicalcium silicate. With the increase of temperature, the increasing trend of liquid amount is obviously weaker than those of slags with low CaO contents. Obviously, high CaO content is not conducive to the formation of liquid phase.

As shown in Fig. 3.14, the excessive CaO will react with olivine. The ferric ion in olivine is replaced and released with the increase in the CaO content. When the CaO content is higher than 23 wt%, a monoxide phase (50–70 wt% FeO) exists (Fig. 3.14f–h). Hence, if the slag is kept in a reducing atmosphere, ferrous oxide will further be reduced to metallic iron.

3.2.2 Effect of FeO Content

Under the CaO contents of 2 wt% and 10 wt%, the designed compositions of slags with various FeO contents are shown in Tables 3.15 and 3.16, respectively. The trends of liquid phase formation with temperature are shown in Figs. 3.15 and 3.16, respectively. It can be found that the FeO content has great influence on the initial temperature for liquid phase formation and the amount of liquid phase at various temperatures. Generally, with increase of FeO content, the initial temperature for the liquid phase formation decreases gradually.

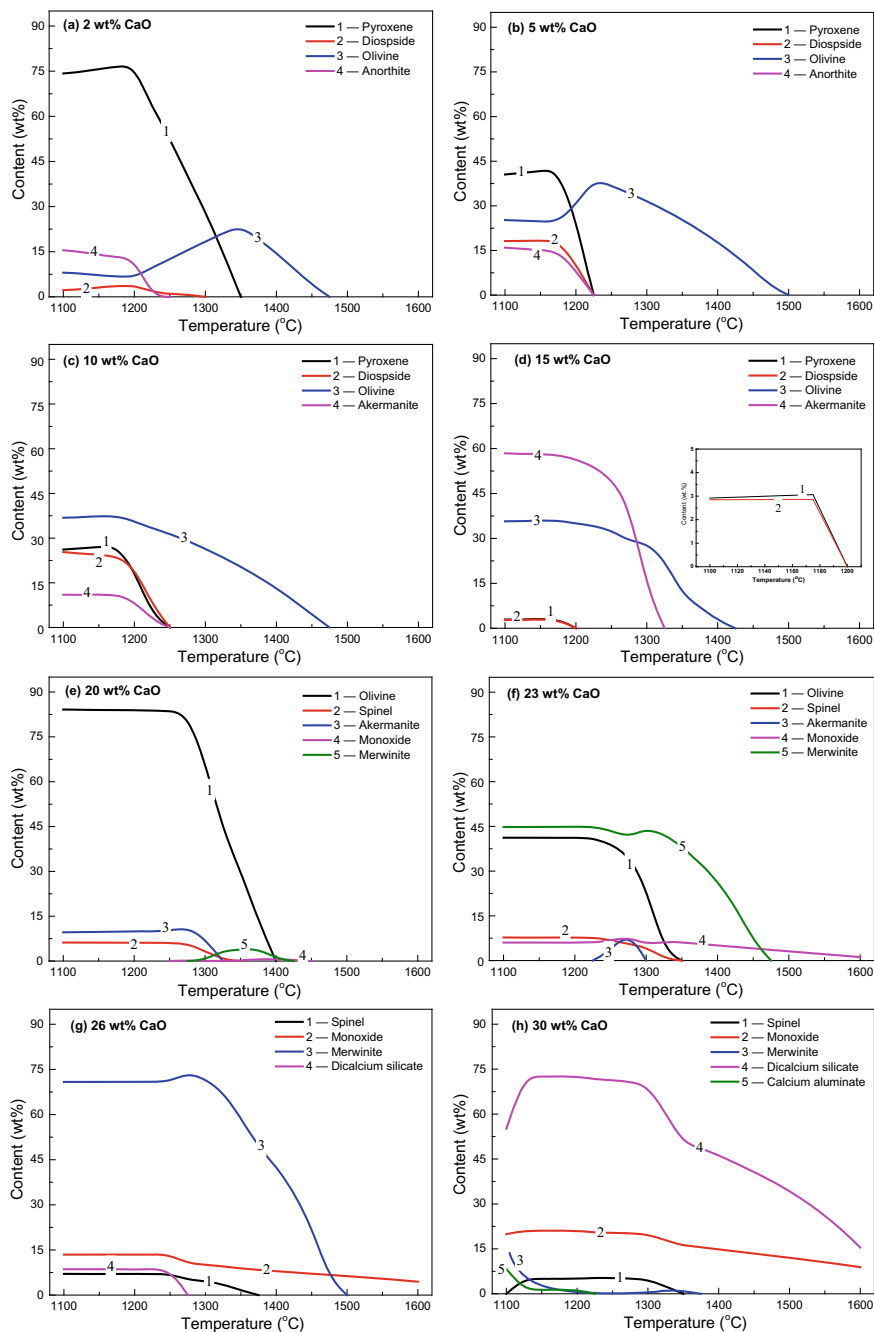


Fig. 3.14 Effect of CaO content on the phase transformation with increasing temperature by fixing FeO content of 10 wt%

Table 3.15 Designed compositions of slags with various FeO contents (CaO content: 2 wt%)

CaO content in mixture (wt%)	Composition of slag (wt%)				
	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃
2.0	0	4.3	57.4	29.0	9.3
2.0	5.0	4.1	54.5	27.6	8.8
2.0	10.0	3.9	51.6	26.1	8.4
2.0	15.0	3.7	48.8	24.7	7.9
2.0	20.0	3.5	45.9	23.2	7.4
2.0	25.0	3.2	43.0	21.8	7.0

Table 3.16 Designed compositions of slags with various FeO contents (CaO content: 10 wt%)

CaO content in mixture (wt%)	Composition of slag (wt%)				
	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃
10.0	0	19.9	48.0	24.3	7.8
10.0	5	18.9	45.6	23.1	7.4
10.0	10	17.9	43.2	21.9	7.0
10.0	15	16.9	40.8	20.6	6.6
10.0	20	15.9	38.4	19.4	6.2
10.0	25	14.9	36.0	18.2	5.8

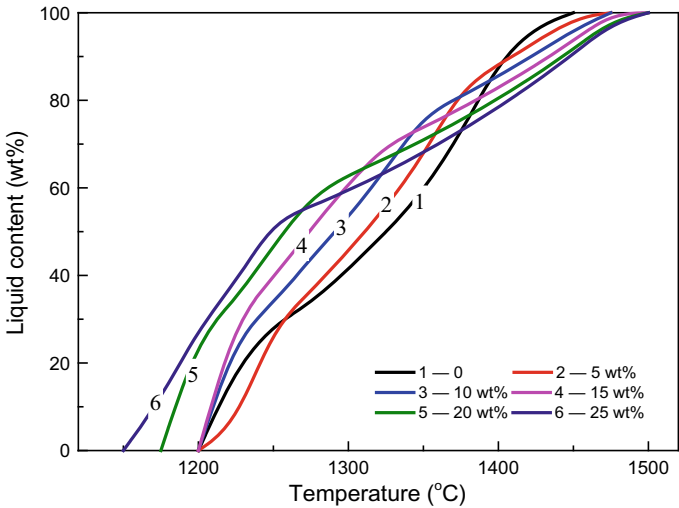


Fig. 3.15 Effect of FeO content on the liquid phase amount with increasing temperature by fixing CaO content of 2 wt%

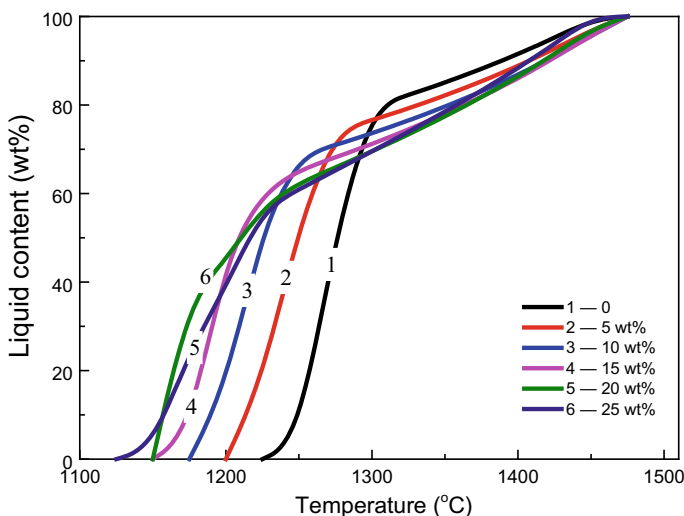


Fig. 3.16 Effect of FeO content on the liquid phase amount with increasing temperature by fixing CaO content of 10 wt%, reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

When the CaO content is 2 wt%, the initial temperature for the liquid phase formation is 1225 °C in the FeO content range of 0–15 wt%. This value decreases to 1200 °C at the FeO content of 20 wt%. When the FeO content increases to 25 wt%, the initial temperature for the liquid phase formation drops to 1175 °C (Fig. 3.15). When the CaO content is 10 wt%, the initial temperature for the liquid phase formation decreases from 1250 °C to 1200 °C when the FeO content increases from 0 to 10 wt%. Further increase of FeO content to 25 wt% leads to decrease of temperature to 1150 °C (Fig. 3.16).

As the CaO content is 2 wt%, the variations of the main phases with FeO content are shown in Fig. 3.17. Pyroxene is the main phase of slag at 1100–1200 °C when the FeO content is in the range 0–5 wt%. There also exist small amounts of diopside, anorthite, cordierite and tridymite. With the increase of temperature, diopside, anorthite, cordierite and tridymite begin to melt and form liquid phase. With further increase of temperature, the melting of pyroxene results in the increase of liquid phase amount.

When the FeO content exceeds 10 wt%, the phases of slag are pyroxene, diopside, anorthite and olivine. The combination of tridymite and excessive FeO forms olivine. Hence, the tridymite disappears. Compared with Fig. 3.17c–f, the amount of pyroxene decreases and the olivine amount increases with increasing FeO content. At temperatures below 1250 °C, the amount of liquid phase increases with increasing FeO content. At this moment, fayalite and olivine are fused. After complete melting of these phases, the increase in the liquid amount depends on melting of forsterite. The amount of forsterite increases with FeO content. Because of its high melting point, it is relatively difficult to melt and form liquid phase. Therefore, the total amount of

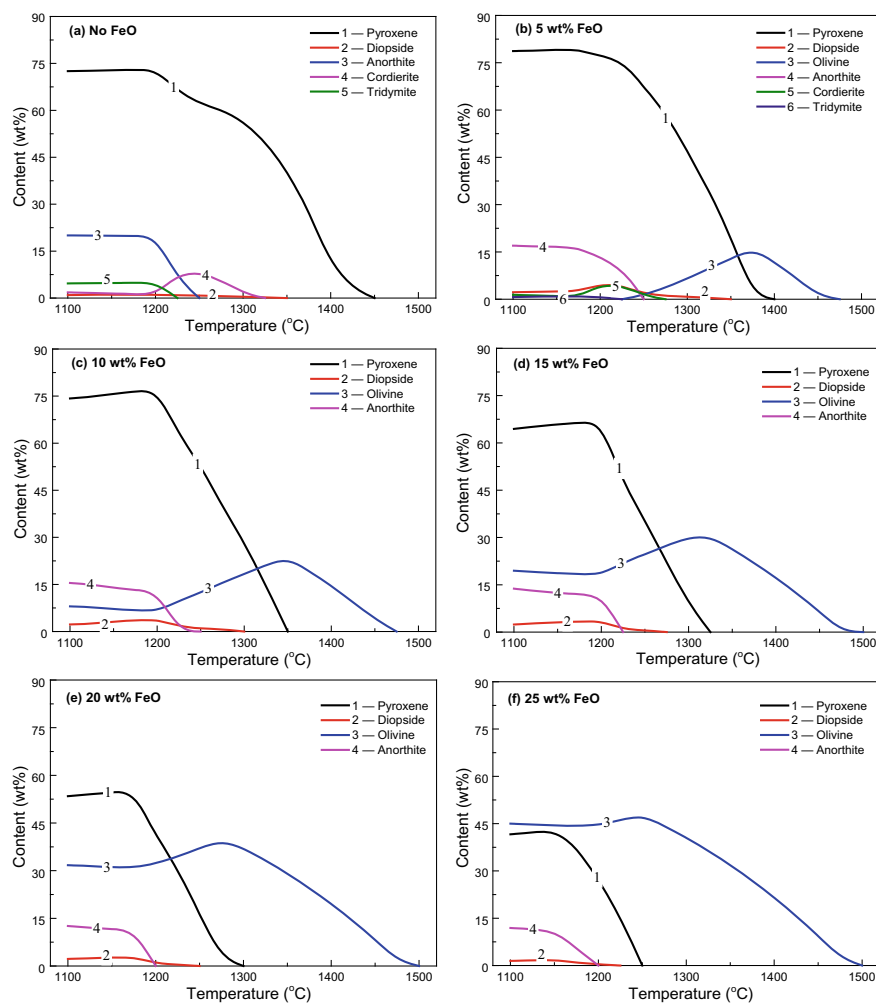


Fig. 3.17 Effect of FeO content on the phase transformation with increasing temperature by fixing CaO content of 2 wt%

liquid phase in the slag with high FeO content is lower than that in the slag with low FeO content at temperatures above 1400 °C (Fig. 3.15).

As shown in Fig. 3.18, when the CaO content is 10 wt%, the initial temperature for the liquid formation changes more significantly with different FeO contents. With the increase of FeO content, the initial temperature for the liquid phase formation decreases. Compared with the case having 2 wt% CaO, increasing CaO content results in the decrease of pyroxene and increase of olivine. The amount of olivine in the slag containing 10 wt% CaO is significantly higher than that in the slag with 2 wt% CaO and the same FeO content. When the FeO is absent (that is, iron oxides are completely

reduced to metallic iron), the increase of CaO content leads to the disappearance of anorthite and cordierite and the initial temperature for the liquid phase formation of slag with CaO content of 10 wt% is higher than that of slag with CaO content of 2 wt%. However, as the FeO content is 10–25 wt%, the initial temperature for the liquid phase formation of slag containing 10 wt% CaO is always lower than that of slag containing 2 wt% CaO (Figs. 3.15 and 3.16). These results confirm that the formation of olivine can promote the formation of liquid phase (Figs. 3.17 and 3.18).

Above all, the main function of ferrous oxide is to decrease initial melting temperature and to increase liquid amount at low temperature (less than 1300 °C). However,

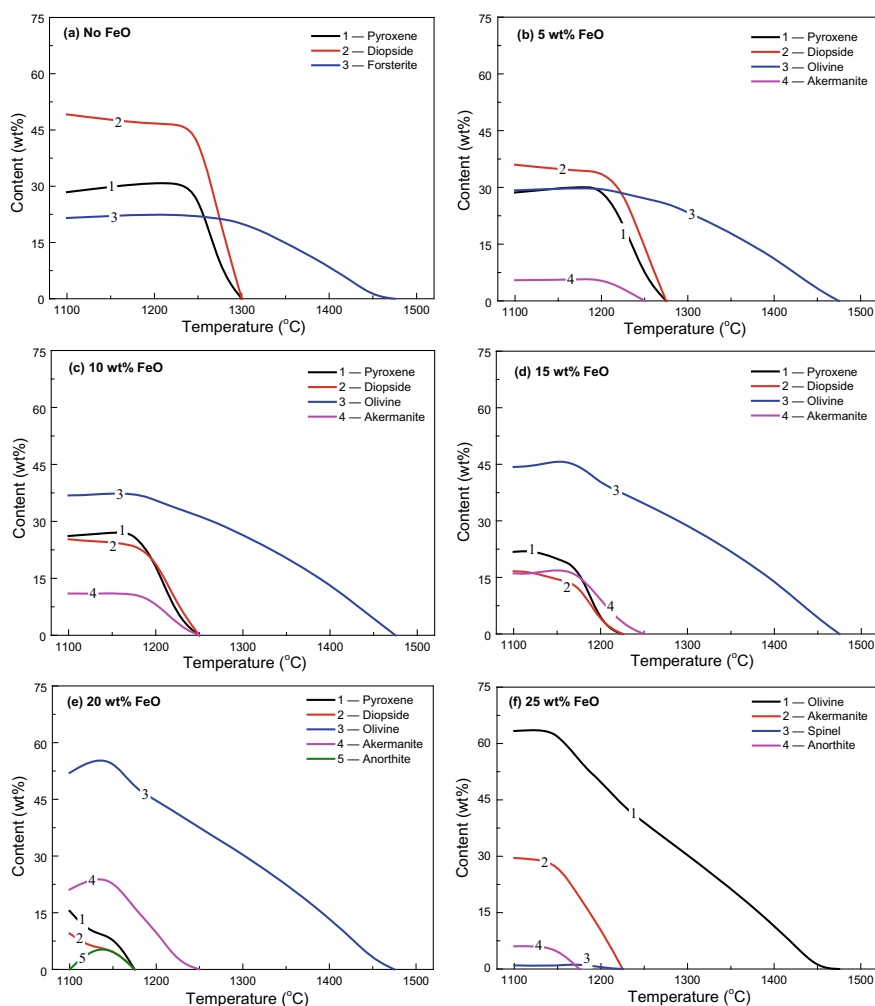


Fig. 3.18 Effect of FeO content on the phase transformation with increasing temperature by fixing CaO content of 10 wt%

the effect of ferrous oxide on the formation of liquid phase is limited at high temperature. The effect of FeO on the formation of liquid phase is mainly due to the formation of olivine. The melting points of fayalite and olivine are relatively low and they can melt at 1200–1300 °C. The increase of ferrous oxide content is conducive to the increase of liquid phase.

3.2.3 Effect of MgO Content

With the specified CaO and FeO contents, the designed compositions of slags with various MgO contents are shown in Tables 3.17 and 3.18, respectively, and the effect of MgO content on the liquid phase amount is shown in Figs. 3.19 and 3.20, respectively.

When the CaO content is 2 wt%, the initial temperature for the liquid phase formation increases with MgO content (Fig. 3.19). When the MgO content reaches 18–30 wt%, the initial temperature for the liquid phase formation is 1175 °C. This temperature increases to 1200 °C as the MgO content was 26 wt%. In addition, the amount of liquid phase decreases with the increasing MgO content at the same temperature.

With the CaO content of 2 wt%, the variations of phases with temperature is shown in Fig. 3.21. At 1100–1175 °C, pyroxene, anorthite and tridymite are the main phases of slag and there also exist small amounts of diopside and cordierite.

Table 3.17 Designed compositions of slags with various MgO contents (CaO content: 2 wt% and FeO content: 10 wt%)

CaO content in the mixture (wt%)	Composition of slag (wt%)				
	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃
2.0	10.0	4.4	58.2	18.0	9.4
2.0	10.0	4.1	54.9	22.0	8.9
2.0	10.0	3.9	51.6	26.0	8.4
2.0	10.0	3.7	48.4	30.0	7.9

Table 3.18 Designed compositions of slags with various MgO contents (CaO content: 10 wt% and FeO content: 10 wt%)

CaO content in the mixture (wt%)	Composition of slag (wt%)				
	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃
10.0	10.0	19.0	45.6	18.0	7.4
10.0	10.0	17.9	43.2	22.0	7.0
10.0	10.0	16.8	40.6	26.0	6.6
10.0	10.0	15.7	38.1	30.0	6.2

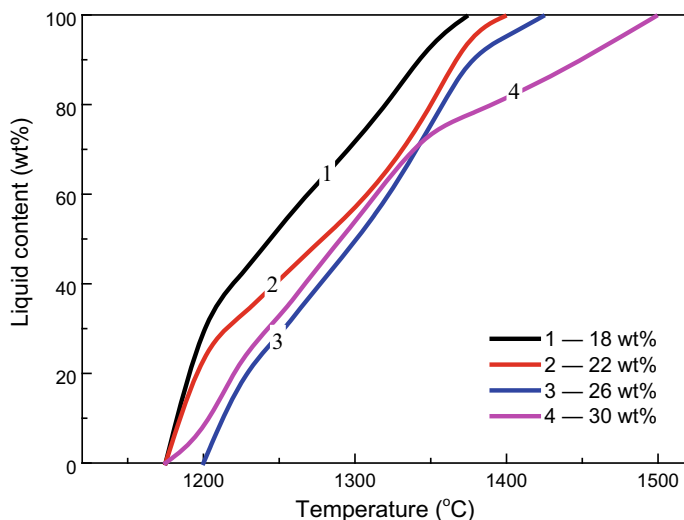


Fig. 3.19 Effect of MgO content on the liquid phase amount with increasing temperature by fixing CaO content of 2 wt% and FeO content of 10 wt%

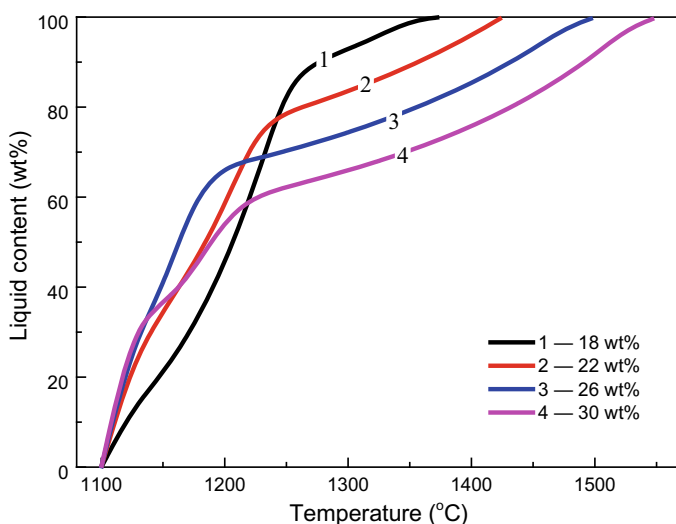


Fig. 3.20 Effect of MgO content on the liquid phase amount with increasing temperature by fixing CaO content of 10 wt% and FeO content of 10 wt%

With the increase of temperature, diopside, anorthite, cordierite and tridymite begin to melt to form liquid phase. Besides, with increasing MgO content, MgO reacts with tridymite to form pyroxene and forsterite with high melting points, which leads to the decrease of liquid phase at the same temperature.

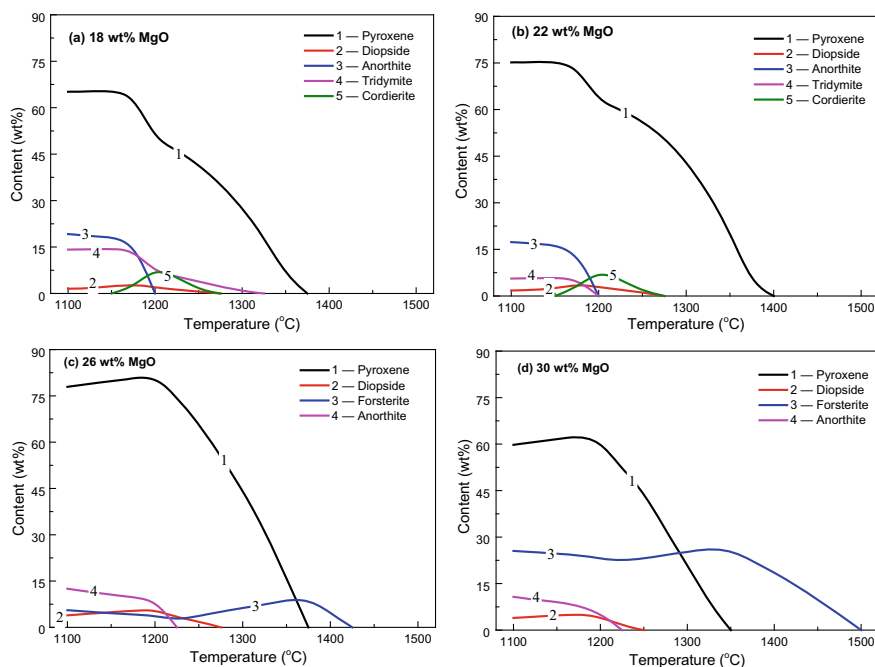


Fig. 3.21 Effect of MgO content on the phase transformation with increasing temperature by fixing CaO content of 2 wt% and FeO content of 10 wt%

As shown in Fig. 3.20, when the CaO content is 10 wt%, the initial temperature for the liquid phase formation remains stable (1100 °C) with various MgO contents. However, the amount of liquid phase increases with MgO content when the temperature is lower than 1200 °C. When the temperature is higher than 1250 °C, the amount of liquid phase decreases with increasing MgO content at the same temperature.

From Fig. 3.22, when the CaO content reaches 10 wt%, the contents of pyroxene and diopside decrease with the increase in the MgO content, while the contents of forsterite and akermanite increase. With the MgO content of 18 wt%, pyroxene, diopside and forsterite are the main phases in slag at 1100 °C and their contents are 40.9 wt%, 39.7 wt% and 13.6 wt%, respectively. When the MgO content increases to 30 wt%, the contents of pyroxene and diopside decrease to 10.1 wt% and 10.6 wt%, respectively, while the forsterite content increases to 38.5 wt%. When the temperature exceeds 1200 °C, the formation of liquid phase depends on the melting of forsterite. Therefore, the amount of liquid phase decreases with the increase in the MgO content at temperatures above 1250 °C.

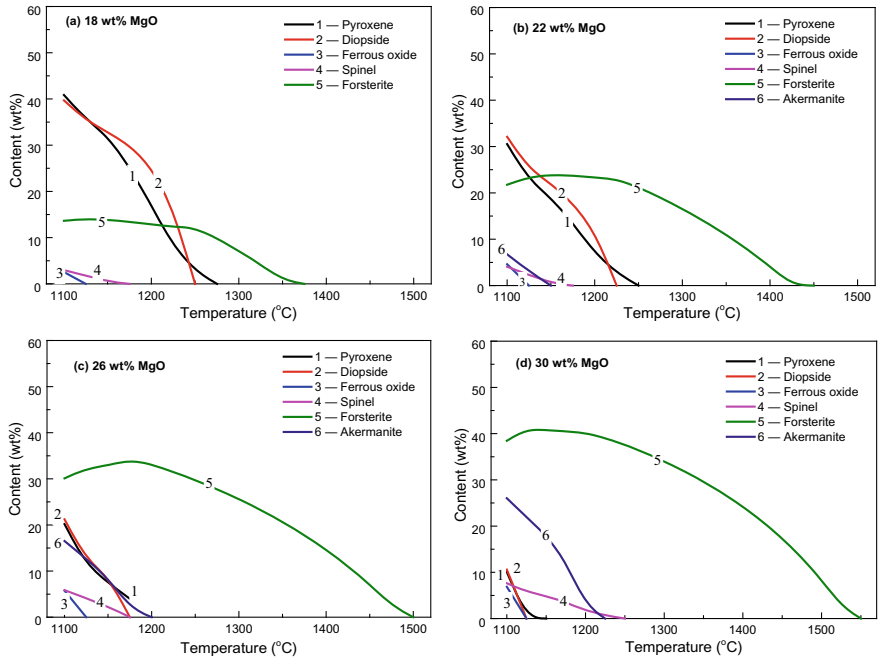


Fig. 3.22 Effect of MgO content on the phase transformation with increasing temperature by fixing CaO content of 10 wt% and FeO content of 10 wt%

3.2.4 Effect of Al_2O_3 Content

The designed compositions of slags with various Al_2O_3 contents are shown in Tables 3.19 and 3.20 and the variation of liquid phase formation with temperature are shown in Figs. 3.23 and 3.24, respectively. The initial temperature for the liquid phase formation decreases with increasing Al_2O_3 content. Meanwhile, at the same temperature, the amount of liquid phase gradually increases with the increase of Al_2O_3 content.

Table 3.19 Designed compositions of slags with various Al_2O_3 contents (CaO content of 2 wt% and FeO content of 10 wt%)

CaO content in the mixture (wt%)	Composition of slag (wt%)				
	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃
2.0	10.0	4.3	56.9	28.8	0.0
2.0	10.0	4.1	54.4	27.5	4.0
2.0	10.0	3.9	51.9	26.2	8.0
2.0	10.0	3.7	49.3	25.0	12.0
2.0	10.0	3.5	46.8	23.7	16.0

Table 3.20 Designed compositions of slags with various Al₂O₃ contents (CaO content of 10 wt% and FeO content of 10 wt%)

CaO content in the mixture (wt%)	Composition of slag (wt%)				
	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃
10.0	10.0	19.4	46.9	23.7	0.0
10.0	10.0	18.6	44.8	22.7	4.0
10.0	10.0	17.7	42.7	21.6	8.0
10.0	10.0	16.8	40.6	20.5	12.0
10.0	10.0	16.0	38.5	19.5	16.0

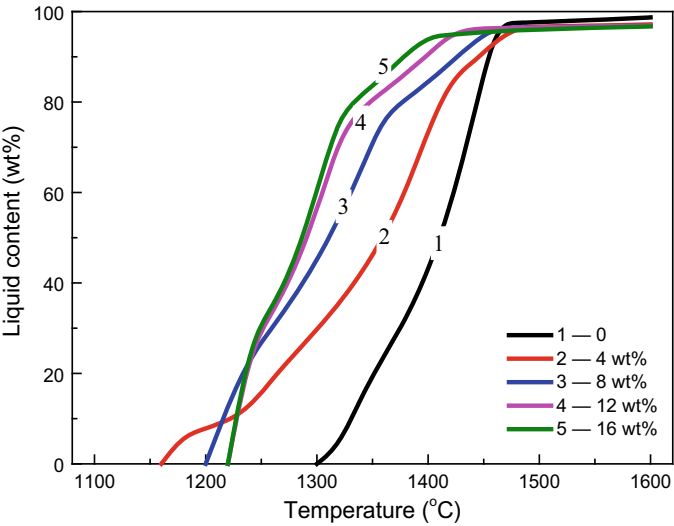


Fig. 3.23 Effect of Al₂O₃ content on the liquid phase amount with increasing temperature by fixing CaO content of 2 wt% and FeO content of 10 wt%

With the CaO content of 2 wt%, the initial temperature for the liquid phase formation reaches 1300 °C in the absence of Al₂O₃ content. This temperature decreases to 1200 °C when the Al₂O₃ content is 8 wt%. There is a similar trend with the CaO content of 10 wt%. The initial temperature for the liquid phase formation is 1275 °C in the absence of Al₂O₃, while it decreases to 1175 °C in the presence of 8 wt% Al₂O₃. With further increase in the Al₂O₃ content, the trend of liquid phase formation is basically the same as that when the temperature changes.

The phase transformations of slags with different Al₂O₃ contents are shown in Figs. 3.25 and 3.26, respectively. When the given CaO content is 2 wt%, pyroxene is the main phase of slag with different Al₂O₃ contents and the proportion of pyroxene is more than 70 wt% before melting. There also exist diopside, anorthite, olivine, cordierite and tridymite in the slag. With the increase of temperature, diopside, anorthite, cordierite and tridymite melt firstly to form liquid phase. When the Al₂O₃ is

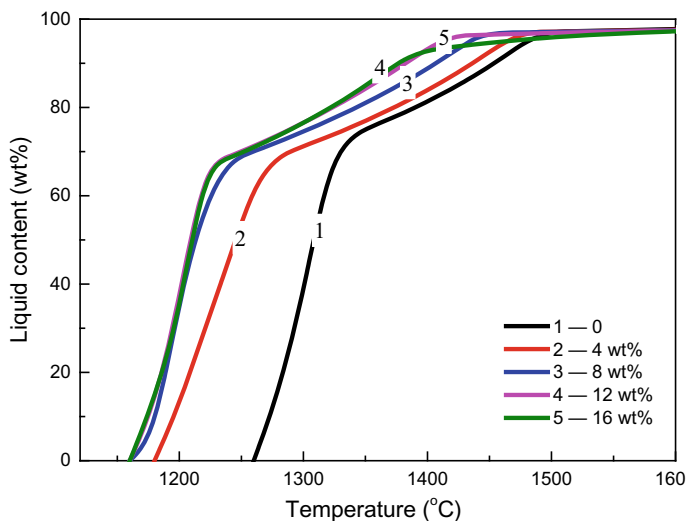


Fig. 3.24 Effect of Al_2O_3 content on the liquid phase amount with increasing temperature by fixing CaO content of 10 wt% and FeO content of 10 wt%

absent, only diopside melts to form liquid phase, which leads to high initial temperature for the liquid phase formation (Figs. 3.23 and 3.25a). In the presence of Al_2O_3 , diopside, anorthite and cordierite form solid solution with low melting point, which reduces the melting temperature of slag. As a result, the initial temperature for the liquid phase formation decreases (Fig. 3.23).

When the CaO content reaches 10 wt%, the content of pyroxene decreases obviously, while the contents of diopside and olivine increase. Besides, akermanite appears (Fig. 3.26). In the absence of Al_2O_3 , the amounts of diopside, akermanite and olivine are 36 wt%, 20 wt% and 34 wt%, respectively. With the increase of Al_2O_3 content, the contents of diopside and akermanite decrease gradually, while the pyroxene content increases gradually. The amount of olivine increases firstly and then decreases. For example, with the Al_2O_3 content of 16 wt%, the contents of diopside and olivine are 29 wt% and 28 wt%, respectively, and the akermanite disappears.

With different Al_2O_3 contents, the initial liquid phase is mainly formed by melting of diopside and olivine. However, with the increase of Al_2O_3 content, the eutectic point gradually decreases, which results in the decrease of initial temperature for the liquid phase formation. At temperatures above 1300 °C, the liquid phase forms due to melting of olivine and spinel. At this moment, the trend of liquid phase formation slows down with increasing temperature.

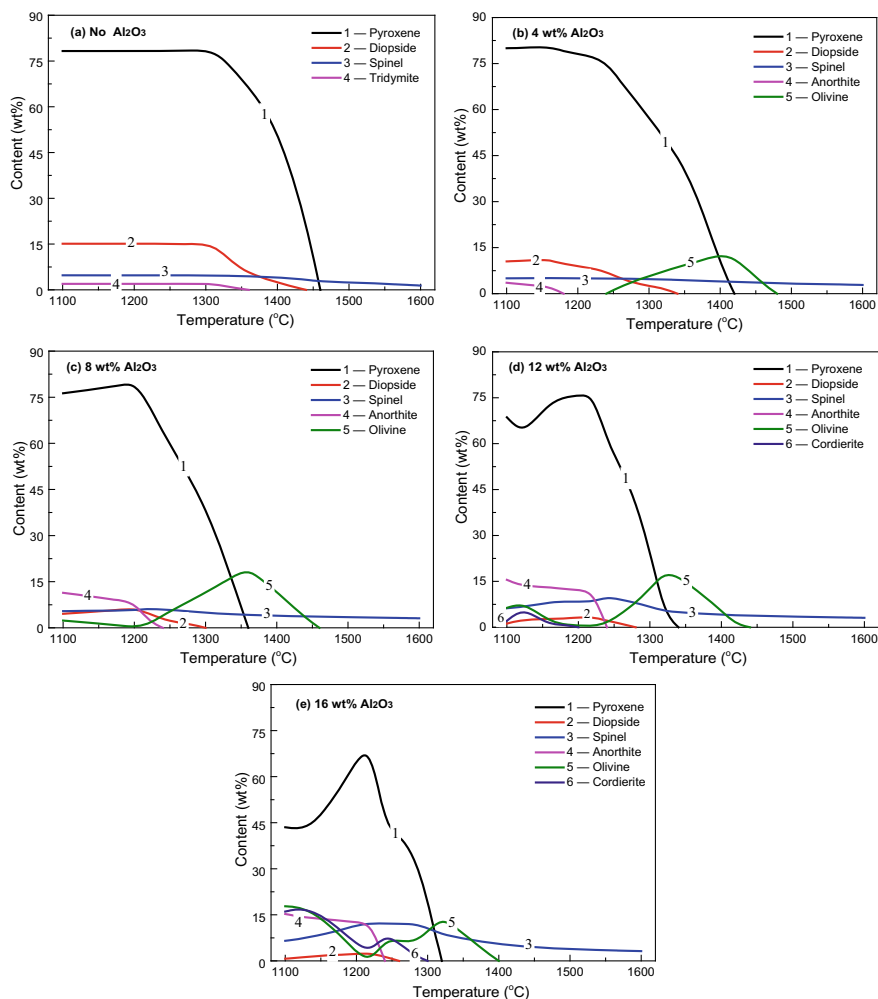


Fig. 3.25 Effect of Al_2O_3 content on the phase transformation with increasing temperature by fixing CaO content of 2 wt% and FeO content of 10 wt%

3.3 Viscosity Behavior of Slag

The viscosity is one of the most important properties of smelting slag. The value of viscosity can be used to evaluate the fluidity of molten slag. After melting of laterite ore, the viscosity of slag has a significant impact on the separation of molten metal from slag. In addition, the viscosity of slag has an effect on the temperature distribution in electric furnace. Generally, the upper limit of the viscosity for separation of hot metal from slag during smelting is 1.0 Pa·s. A high viscosity of slag limits the hot metal separation, leading to a low metal recovery. The regulation of

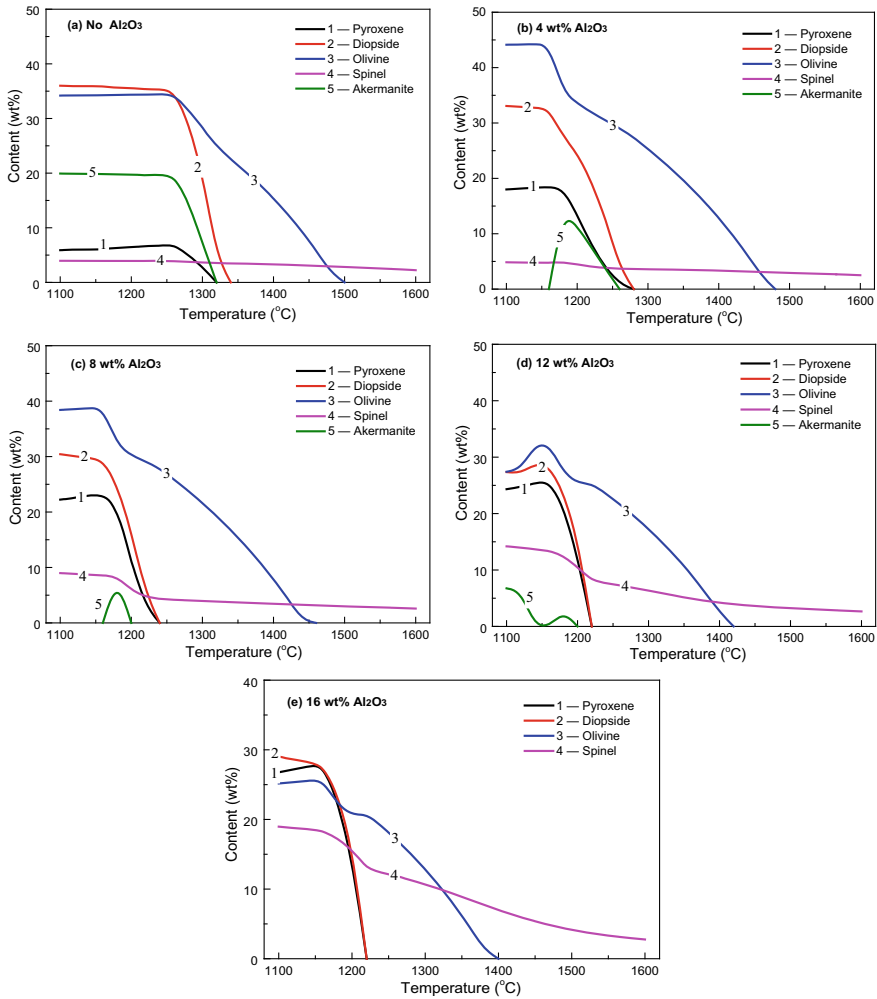


Fig. 3.26 Effect of Al_2O_3 content on the phase transformation with increasing temperature by fixing CaO content of 10 wt% and FeO content of 10 wt%

the slag constituents is a cost-effective route for decreasing the viscosity of slag at relatively low smelting temperatures. The contents of MgO , Al_2O_3 , CaO and FeO in laterite ore have obvious influence on the viscosity of slag during ferronickel production.

3.3.1 Effect of CaO Content

According to the compositions of slags with various CaO contents (Table 3.14), the corresponding viscosity values can be calculated based on the Einstein-Roscoe equation (Eq. 3.1) [26] and the results are shown in Fig. 3.27.

$$\text{Viscosity}_{(\text{solid+liquid mixture})} \approx \text{Viscosity}_{(\text{liquid})} \times (1 - C_{(\text{solid fraction})})^{-2.5} \quad (3.1)$$

where $\text{Viscosity}_{(\text{solid+liquid mixture})}$ is the viscosity of slag at a given temperature, Pa·s; $\text{Viscosity}_{(\text{liquid})}$ is the viscosity of the liquid phase in slag at a given temperature, Pa·s, and $C_{(\text{solid fraction})}$ is the proportion of solid phase in slag at a given temperature, wt%.

With the FeO content of 10 wt%, as the CaO content increases, the viscosity of slag decreases firstly and then increases at temperatures below 1400 °C. Especially, the viscosity decreases obviously in the CaO content range 10–23 wt%. With the CaO content of 2 wt%, the viscosity of slag is 2.0 Pa·s at 1400 °C. The viscosity decreases to 1.1 Pa·s at 1320 °C when the CaO content increases to 15 wt%. The results show that increasing CaO content is beneficial to the improvement of fluidity and to decrease of smelting temperature of slag. Further increasing CaO content will have an adverse effect on the viscosity of slag. With the CaO content of 30 wt%, the slag viscosity reaches 2.3 Pa·s at 1400 °C, which exceeds the viscosity of slag with the CaO content of 2 wt%. To make its viscosity lower than 1 Pa·s, the temperature is required to be above 1440 °C. As shown in Fig. 3.27, the optimal CaO content is in the range 10–23 wt%. Under these conditions, the slag viscosity can be obtained by

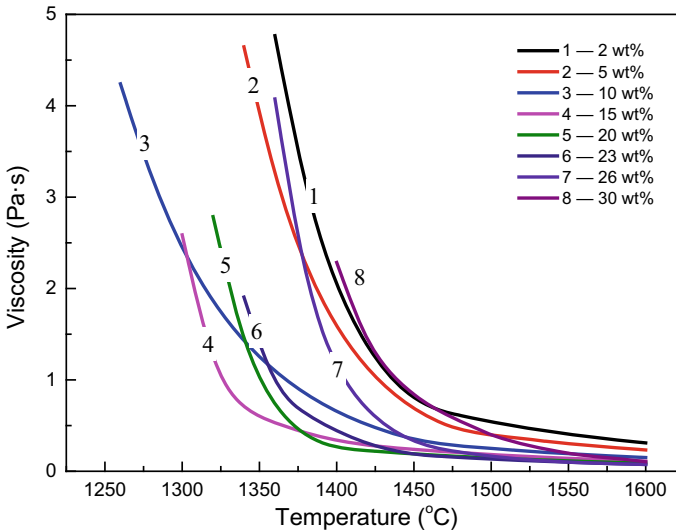


Fig. 3.27 Effect of CaO content on the viscosity of slag by fixing FeO content of 10 wt%

controlling the temperature in the range 1320–1360 °C. Compared with the smelting temperature of the slag with CaO content of 2 wt%, the smelting temperature of the slag with the optimal CaO content can be reduced by 80–120 °C.

3.3.2 Effect of FeO Content

Figures 3.28 and 3.29 show the influence of FeO content on the viscosity of slag with CaO contents of 2 wt% and 10 wt%, respectively. The designed compositions of slags are shown in Tables 3.15 and 3.16, respectively. With the increase of FeO content, the viscosity of slag decreases at a given temperature. With the CaO content of 2 wt%, the temperature required for the viscosity to reach 1.2 Pa·s is 1500 °C in the absence of FeO. When the FeO content reaches 15 wt% and 25 wt%, the required temperature is only 1420 °C and 1380 °C, respectively, and the viscosity of slag decreases to about 1.0 Pa·s.

With the CaO content of 10 wt%, the viscosity of slag will be reduced compared with that of slag containing 2 wt% CaO. However, the improvement of slag viscosity by FeO is still the same. It is necessary to keep the temperature above 1400 °C to ensure the viscosity lower than 1.0 Pa·s in the absence of FeO. When the viscosity is lower than 1.0 Pa·s, the required temperature is only 1340 °C and 1300 °C, respectively, with the FeO contents of 15 wt% and 25 wt%.

It should be noted that the range of FeO content examined in the above calculation of viscosity is large. In the actual smelting process, the total iron content in laterite ore is about 15–30 wt% and the iron recovery in ferronickel is estimated at 60–70 wt%.

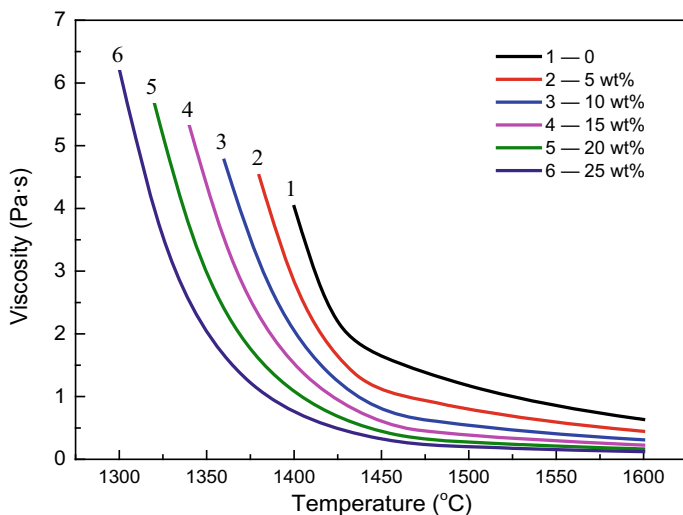


Fig. 3.28 Effect of FeO content on the viscosity of slag by fixing CaO content of 2 wt%

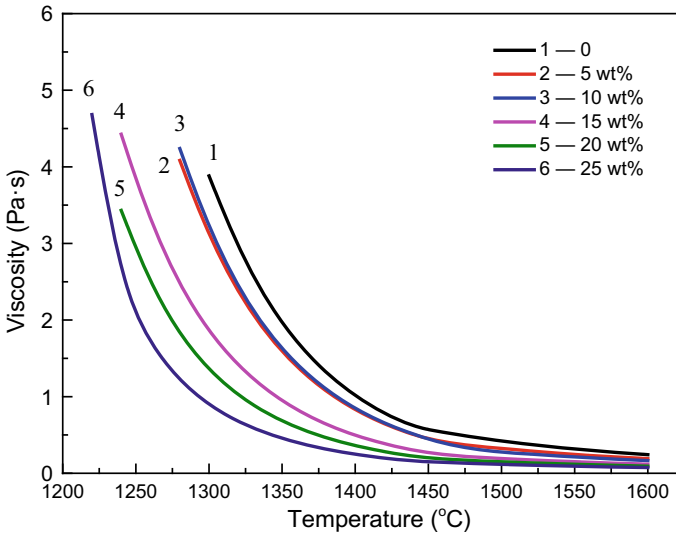


Fig. 3.29 Effect of FeO content on the viscosity of slag by fixing CaO content of 10 wt%

Hence, the FeO content in the final smelting slag rarely exceeds 20 wt% although it can be obtained at the beginning of smelting.

3.3.3 Effect of MgO Content

Figures 3.30 and 3.31 show the effect of MgO content on viscosity of slag and the designed compositions of slag are shown in Tables 3.17 and 3.18, respectively. At the CaO content of 2 wt%, the MgO content has a great effect on the viscosity of slag. At the same temperature, the viscosity decreases with the increase of the MgO content. For example, at the MgO content of 18 wt%, the viscosity of slag is 1.42 Pa·s at temperature of 1500 °C. When the MgO content increases to 30 wt%, the viscosity decreases to 0.35 Pa·s at 1500 °C.

With the CaO content of 10 wt%, the effect of MgO content on the viscosity of slag is obviously reduced. Especially, when the temperature exceeds 1250 °C, the viscosity of slag with different MgO contents is basically the same. At 1325 °C, as the MgO content increases from 18 wt% to 30 wt%, the viscosity of slag is 0.97 Pa·s, 1.02 Pa·s, 1.07 Pa·s and 1.10 Pa·s, respectively.

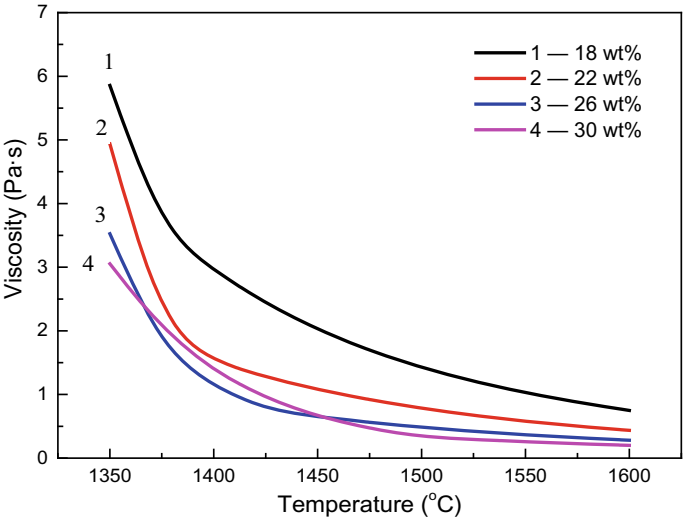


Fig. 3.30 Effect of MgO content on the viscosity of slag by fixing CaO content of 2 wt% and FeO content of 10 wt%

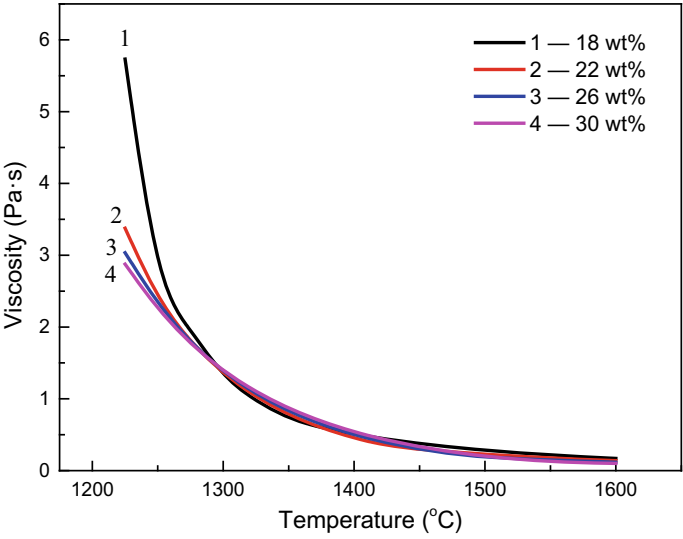


Fig. 3.31 Effect of MgO content on the viscosity of slag by fixing CaO content of 10 wt% and FeO content of 10 wt%

3.3.4 Effect of Al_2O_3 Content

In the $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3$ slag system, increasing Al_2O_3 content is beneficial to the melting property and decrease of the melting temperature of the slag. However, as shown in Figs. 3.32 and 3.33, the increase of Al_2O_3 content has limited influence on the viscosity of slag. With the CaO content of 2 wt% (Fig. 3.32), the Al_2O_3 has a certain effect on the viscosity of the slag when the temperature is lower than 1460 °C. At the same temperature, the slag viscosity decreases with increasing Al_2O_3 content. When the temperature is higher than 1460 °C, the viscosities of slag with different Al_2O_3 contents have little difference.

Table 3.21 shows the variations of liquid phase formation and viscosity of slag with Al_2O_3 content and temperature. The viscosity decreases with the increase of Al_2O_3 content at the same temperature in Figs. 3.32 and 3.33. The increase of Al_2O_3 content is favorable for the liquid phase formation at low temperature, due to the generation of cordierite with low melting point, thus decreasing the viscosity of slag. Compared with the contents of components in liquid phase and the viscosity of slag (Table 3.21), it can be found that the Al_2O_3 content in liquid phase increases with increasing temperature, but the viscosity of slag increases. The main function of Al_2O_3 is to improve the melting property to decrease the slag viscosity. However, the effect of Al_2O_3 on the viscosity of slag after complete melting is limited.

Above all, the viscosity of slag can be effectively decreased by regulating the contents of CaO , MgO , Al_2O_3 and FeO . Compared with the effects of Al_2O_3 and MgO , regulating CaO and FeO contents has more obvious effects on the viscosity of slag.

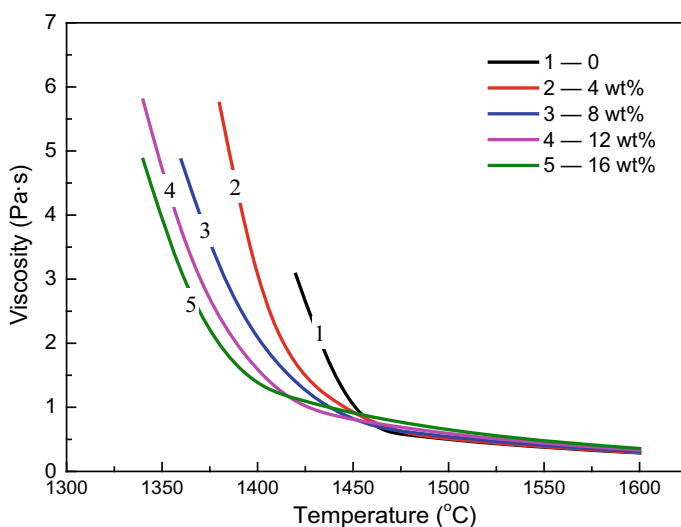


Fig. 3.32 Effect of Al_2O_3 content on the viscosity of slag by fixing CaO content of 2 wt% and FeO content of 10 wt%

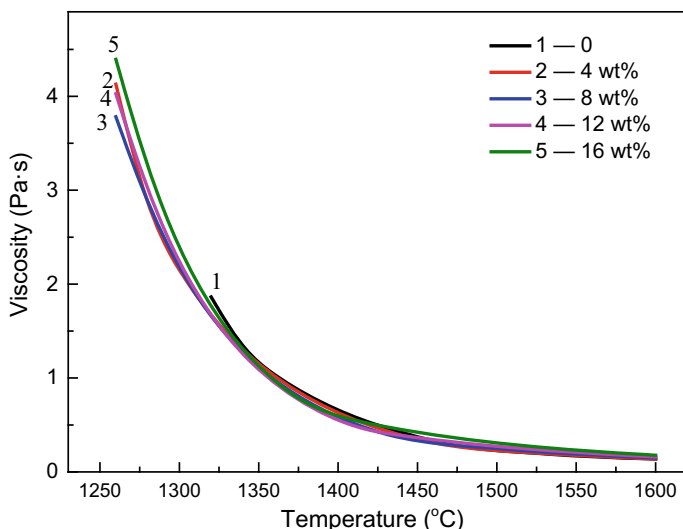


Fig. 3.33 Effect of Al_2O_3 content on the viscosity of slag by fixing CaO content of 10 wt% and FeO content of 10 wt%

3.3.5 Verification Tests

In order to verify the influence of the above components on the slag viscosity, the actual smelting slags with different compositions (Table 3.22) were prepared. The viscosity of the slag was measured using the rotating cylinder method. The schematic illustration of the viscosity measurement system is shown in Fig. 3.34. In each trial, 200 g of pulverized slag was introduced into a molybdenum crucible (inner diameter of 50 mm) inside a corundum crucible (inner diameter of 55 mm), and then placed in a tube furnace filled with argon gas supplied at a flow rate of 1.5 L/min. The furnace was heated to temperature of 1550 °C for 120 min to homogenize the slag. A detector (outer diameter of 15 mm) was immersed into the molten slag to determine the viscosity. The rotation speed of the detector was maintained at 12 rpm. Subsequently, the temperature was decreased every 5 °C with equilibration time of 30 min to further measure the viscosity at different temperatures.

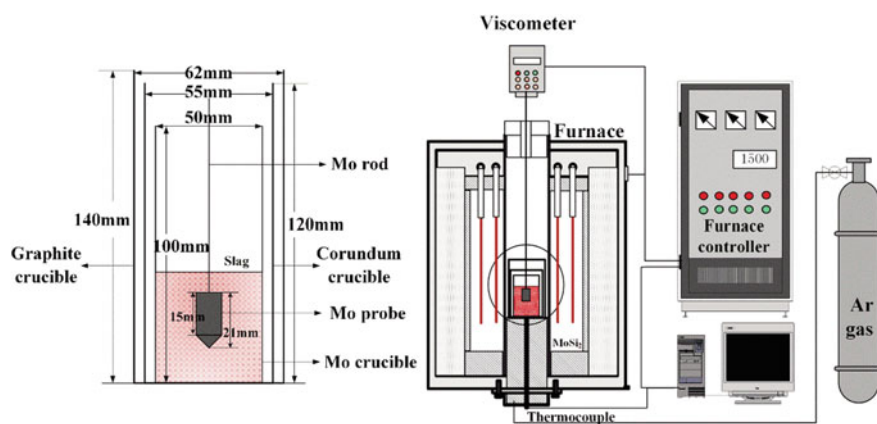
Figure 3.35 shows that the viscosity of slag decreased with increasing CaO content. When the CaO content was 2.0 wt%, the viscosity decreased gradually from 2.4 to 1.1 Pa·s with increasing temperature from 1400 to 1500 °C. The trend of this curve indicated that the smelting slag was acidic. The temperature should exceed 1500 °C to yield an appropriate viscosity of slag containing 2.0 wt% CaO. This value declined sharply with increasing temperature of the slag with higher CaO contents. For the slag containing 12.0 wt% CaO, the viscosity declined rapidly to 0.98 Pa·s at 1410 °C. A further increase of CaO content to 24.0 wt% produced a viscosity of 0.83 Pa·s at 1350 °C.

Table 3.21 Variations of liquid phase formation and viscosity of slag with Al₂O₃ content and temperature

Mixtures		Main component of liquid phase (wt%)					Temperature (°C)	Liquid amount (wt%)	Liquid viscosity (Pa·s)	Slag viscosity (Pa·s)
CaO (wt%)	Al ₂ O ₃ (wt%)	FeO	SiO ₂	MgO	Al ₂ O ₃	CaO				
2	0	12.8	56.0	21.4	0.0	8.3	1400	42.3	0.89	7.6
	8	10.1	53.3	22.2	9.3	4.5		84.4	1.33	2.0
	16	10.1	47.6	22.9	15.4	3.6		94.4	1.15	1.3
2	0	10.1	56.2	28.0	0	4.3	1460	97.4	0.59	0.63
	8	9.9	51.7	25.5	8.2	3.9		96.4	0.64	0.70
	16	10.0	47.0	22.9	15.9	3.6		95.6	0.76	0.85
10	0	12.7	46.7	12.6	0	27.6	1300	38.0	0.68	7.7
	8	9.7	42.9	13.1	10.1	23.9		74.5	1.03	2.2
	16	10.3	41.2	13.2	13.9	21.3		76.5	1.21	2.4
10	0	9.9	47.3	18.0	0	24.1	1400	81.3	0.39	0.65
	8	10.0	42.2	18.1	8.7	20.5		88.8	0.43	0.58
	16	10.2	39.5	18.2	14.0	17.8		93.0	0.49	0.59

Table 3.22 Main chemical compositions of smelting slags prepared from laterite ore-A

No.	Chemical composition (wt%)				
	FeO	CaO	MgO	Al ₂ O ₃	SiO ₂
1	8.1	2.0	25.7	8.2	41.7
2	4.7	12.0	22.4	8.5	36.5
3	2.7	24.0	20.8	6.3	33.6
4	9.2	14.1	21.3	6.5	34.8
5	2.5	13.7	23.9	7.5	38.9
6	8.5	2.4	23.8	10.9	38.9
7	2.5	13.7	22.5	10.3	36.5

**Fig. 3.34** Schematic illustration of the viscosity measurement system [22, 23]

Generally, the upper limit of the viscosity for separating slag and molten metal during smelting is set as 1.0 Pa·s. When the CaO content increased from 2 wt% to 12 wt% and 24 wt%, the smelting temperature of the slag decreased from 1500 °C to 1410 °C and 1350 °C, respectively. The smelting temperature was decreased by 90 °C and 150 °C, respectively. The results were consistent with the theoretical results in Sect. 3.2.1.

Tests 2, 4 and 5 in Table 3.22 show the chemical compositions of slags after smelting with different coke additions. The main difference was the FeO content, which was caused by different degree of iron oxide reduction. Figure 3.36 shows that the viscosity exhibited a downward trend with increasing FeO content. At temperatures below 1420 °C, the effect of FeO on the viscosity was more significant than that at temperatures above 1420 °C. For example, at 1410 °C, the viscosities of slags with the FeO contents of 2.5 wt%, 4.7 wt% and 9.2 wt% were 1.95 Pa·s, 0.98 Pa·s and 0.64 Pa·s, respectively (Fig. 3.26). When the temperature reached 1500 °C, these viscosities were very close, namely 0.54 Pa·s, 0.46 Pa·s and 0.40 Pa·s, respectively.

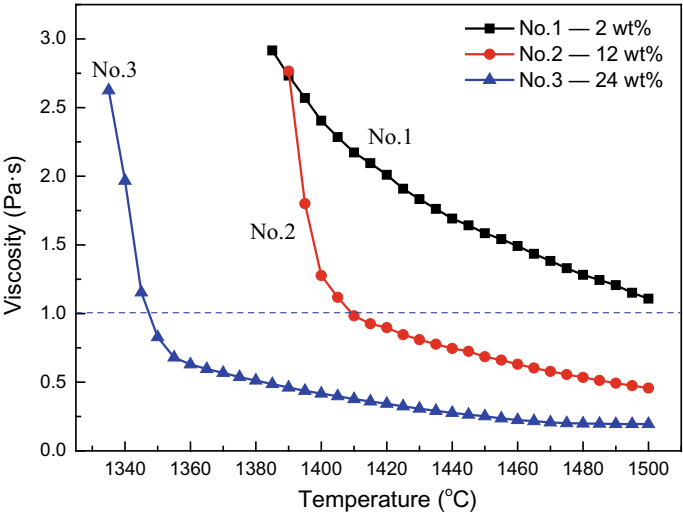


Fig. 3.35 Viscosities of slags with various CaO contents, reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

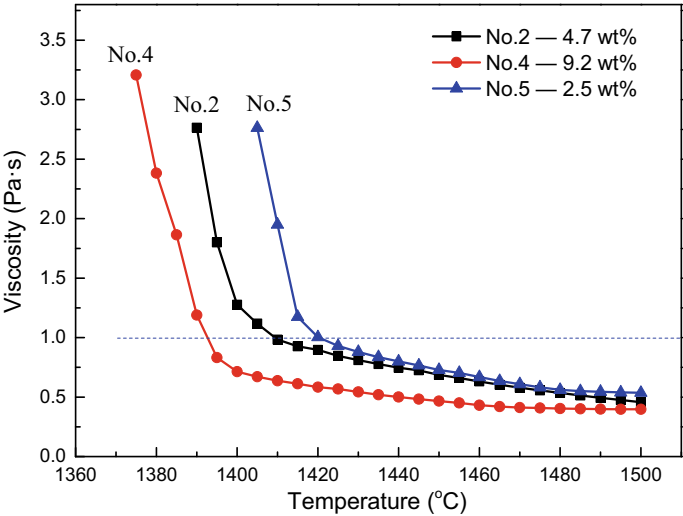


Fig. 3.36 Viscosities of slags with various FeO contents, reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

The smelting temperature required for slag could be reduced by properly increasing the FeO content. When the FeO content of slag was 2.5 wt%, it is necessary to keep the temperature above 1420 °C to ensure satisfied fluidity of slag. As the FeO content increased to 9.2 wt%, the lower limit of smelting temperature was reduced to 1395 °C. In the smelting process, the FeO content in slag could be controlled by regulating the iron content of raw materials and the coke addition.

With the fixed CaO content, the viscosity declined with increasing content of Al_2O_3 at given temperatures (Figs. 3.37 and 3.38). With CaO content of approximately 2.0 wt%, the viscosity decreased from 1.1 Pa·s at 1500 °C to 1.0 Pa·s at 1470 °C with the increase of Al_2O_3 content from 8.2 wt% to 10.9 wt% (Fig. 3.37). When the CaO content increased to approximately 12 wt%, the viscosity decreased more drastically. The satisfactory values were obtained at low temperatures: 0.98 Pa·s at 1410 °C (8.5 wt% of Al_2O_3) and 0.95 Pa·s at 1380 °C (10.3 wt% of Al_2O_3) (Fig. 3.38).

As shown in Fig. 3.38, after addition of CaO, the viscosity of slag with different Al_2O_3 contents tended to be consistent with increasing temperature. At 1400 °C, the viscosities of the slags reached 1.28 Pa·s and 0.51 Pa·s, respectively, with Al_2O_3 contents of 8.5 wt% and 10.3 wt%. These viscosities were 0.46 Pa·s and 0.41 Pa·s, respectively, when the temperature increased to 1500 °C. At this moment, the viscosity was basically the same. The results were similar to the calculated results of viscosity.

In summary, the viscosity of slag could be decreased by controlling the contents of its constituents. The lower limit of smelting temperature could reach about 1380 °C. However, it should be noted that the temperature required for melting of ferronickel

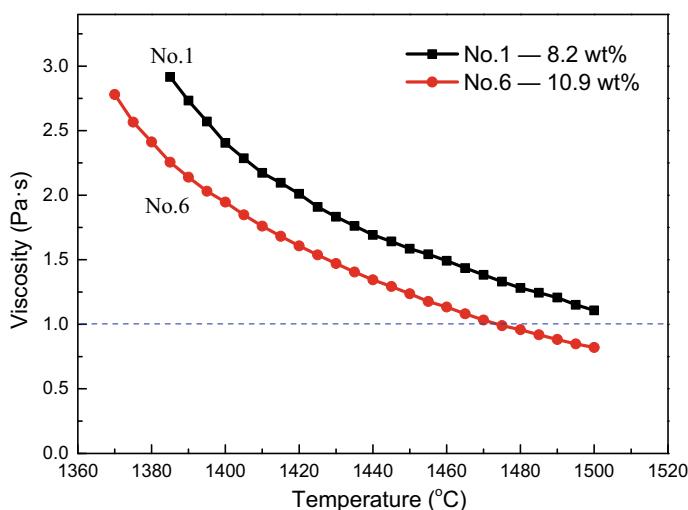


Fig. 3.37 Viscosities of slags with various Al_2O_3 contents by fixing CaO content of nearly 2 wt%, reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

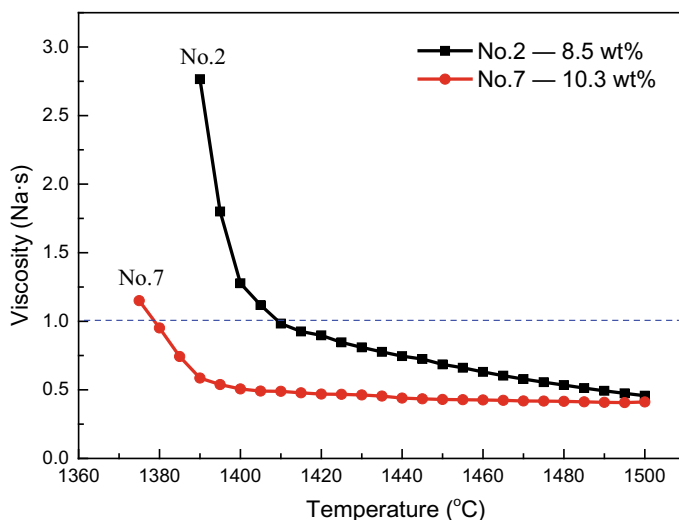


Fig. 3.38 Viscosities of slags with various Al_2O_3 contents by fixing CaO content of nearly 13 wt%, reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

should also be met in the actual smelting process. In ironmaking process, the temperature of molten iron has an obvious effect on its high temperature fluidity and subsequent separation from slag. The melting temperature of molten iron is greatly affected by the contents of silicon, carbon, chromium and other impurities in the molten iron. The temperature of molten iron in production is generally required to be 1400–1500 °C, sometime exceeding 1500 °C. On the other hand, the molten iron temperature is 30–50 °C lower than the slag temperature during smelting. Therefore, in order to meet the requirement for producing molten ferronickel, the temperature in electric furnace would be higher than the required temperature of slag.

3.4 Technics for Controlling Slag Formation

In the smelting process of ferronickel, the feeds should be completely melted with the suitable viscosity of slag. Due to the specific characteristics of laterite ore with low iron content, high SiO_2 and MgO contents, a large number of phases with high melting point are formed in the high temperature process, which are difficult to form liquid phase. On the other hand, a large amount of slag is produced, causing the high smelting temperature and high energy consumption.

The above fundamental analysis showed that the composition of slag has an important effect on its melting and viscosity behaviors. Controlling slag formation by regulating the composition of slag is an effective means to reduce the smelting temperature and to decrease the energy consumption required for ferronickel smelting. However,

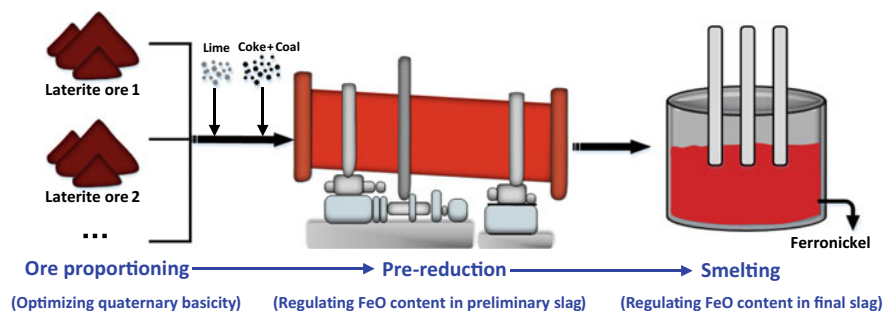


Fig. 3.39 Principle of controlling slag formation, reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

in current RKEF processes, only the MgO/SiO_2 mass ratio is controlled in the range 0.50–0.65 via mixing various types of laterite ores, while the effects of contents of Al_2O_3 , FeO and CaO in the slag are not taken into consideration, which is difficult to guide the production effectively.

The basicity (typically binary basicity, $R_2 = m(\text{CaO})/m(\text{SiO}_2)$) is used for assessing a slag system in ironmaking. The similar techniques can be used in ferronickel-making. Considering all the effects of CaO , MgO , SiO_2 , Al_2O_3 , and FeO on the smelting properties of slag, the regulation method can be improved through the coordination of the quaternary basicity [$R_4 = m(\text{CaO} + \text{MgO})/m(\text{SiO}_2 + \text{Al}_2\text{O}_3)$] and FeO content (Fig. 3.39). It represents an improvement over current systems which solely regulate the MgO/SiO_2 mass ratio. The specific details are as follows:

- (I) Optimization of the quaternary basicity of the slag: various laterite ores are used for regulating the MgO/SiO_2 mass ratio and Al_2O_3 content before being charged into the kiln. A suitable addition of limestone/quicklime, represented as the CaO content, is evaluated. The required quaternary basicity of the slag (Table 3.23) could be determined due to retention in slag.
- (II) Regulating the FeO content in the preliminary slag: during reductive roasting of laterite ore, the atmosphere is controlled in order to produce a suitable amount of FeO in the calcine (known as the preliminary slag). The atmosphere can be strengthened by adding bitumite because it had a higher volatile matter content than coke. The introduction of exhaust gases produced in the electric furnace is also feasible.
- (III) Regulating the FeO content in the final slag: the FeO content in the final slag is controlled via adding semicoke/coke, which is mixed with dried feeds before reductive roasting in the kiln. It is then consumed in the smelting process.

With the above operations, the slag system can be optimized. The acceleration of the melting rate of the pre-reduced feed can be expected owing to the formation of diopside and olivine eutectics during the reduction process. Decreasing the smelting temperature of slag is also practical in the electric furnace. Both these methods help

Table 3.23 Contents of various components for liquidus temperature below 1500 °C

Slag system	MgO/SiO ₂ mass ratio	Quaternary basicity R_4
CaO–MgO–SiO ₂ –8 wt% Al ₂ O ₃ –10 wt% FeO	0.40–0.65	0.59–0.72

reduce the amount of energy required for ferronickel smelting and the improvement of the metals recovery.

3.5 Applications of Controlling Slag Formation

The laboratory-scale tests were carried out for optimization of main parameters, such as coke addition, quaternary basicity of slag, smelting temperature and time. The main chemical composition of laterite-A is shown in Table 3.12 and the results of the proximate analysis of semicoke-A and its ash composition are shown in Table 3.24.

Figure 3.40 shows the flowsheet of the reductive roasting–smelting process. In the laboratory-scale tests, a self-designed rotating tube with an internal diameter of 130 mm and an internal length of 200 mm was used and the reduction temperature was monitored using a thermocouple (see Ref. [27]). The laterite-A mixed with the specified amounts of semicoke-A was reduced at 950 °C for 2 h. The rotational speed of the tube was 5 rpm. The reduced laterite ore containing the given amounts of quick lime of analytical grade was then introduced into a crucible (a volume of 500 mL) for smelting in a vertical resistance furnace. The grades and recovery percentages of iron and nickel in ferronickel were considered.

3.5.1 Effect of Coke addition

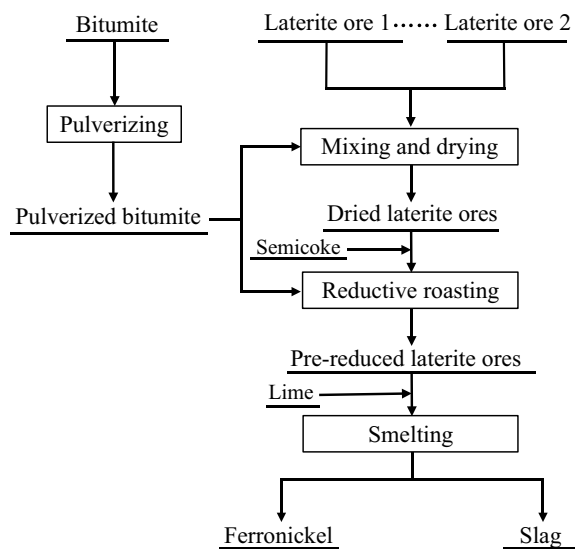
A proportion of semicoke powder was added into laterite ore for pre–reductive roasting. The metallization degrees of iron and nickel oxides and residual carbon content in the calcine are shown in Fig. 3.41. With the increase of semicoke addition from 5.5 wt% to 9.5 wt%, the metallization degree of nickel increased from 58.7 to 77.0% and the metallization degree of iron increased from 8.2 to 15.4%. With the further increase of semicoke addition, there was little influence on the metallization

Table 3.24 Proximate analysis of semicoke-A and its ash composition (wt%)

Proximate analysis				Chemical composition of ash				
F _{Cad}	V _{daf}	A _d	M _{ad}	TFe	SiO ₂	CaO	Al ₂ O ₃	MgO
79.2	2.9	16.8	1.1	20.1	36.4	9.4	21.4	1.2

F_{Cad}: Fixed carbon content; V_{daf}: Volatile matter content; A_d: Ash content; M_{ad}: Moisture content

Fig. 3.40 Flowsheet of reductive roasting followed by smelting of laterite ore



degrees of nickel and iron, but the amount of residual carbon in reduced calcine increased. With the increase of semicoke from 5.5 wt% to 11.5 wt%, the amount of carbon residue increased from 4.9 wt% to 9.2 wt%. This residual carbon would be used for subsequent smelting tests.

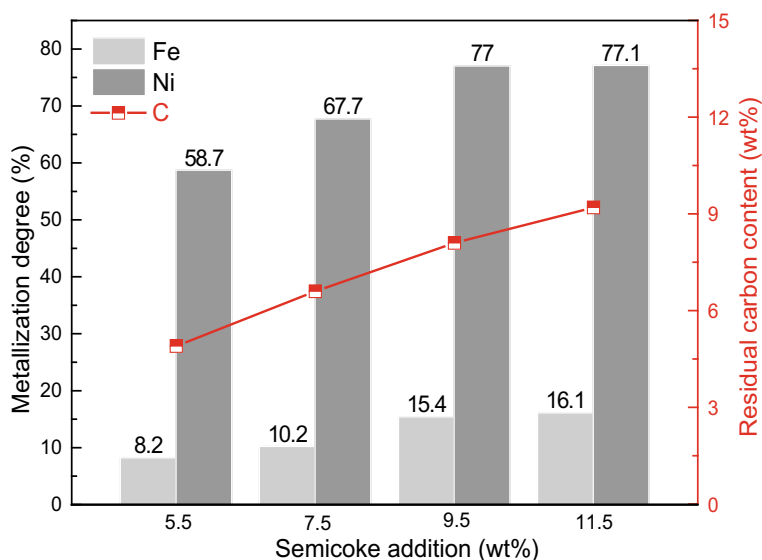


Fig. 3.41 Metallization degrees of iron and nickel and residual carbon contents in the calcine with various semicoke additions by fixing reduction temperature of 950 °C and time of 2 h

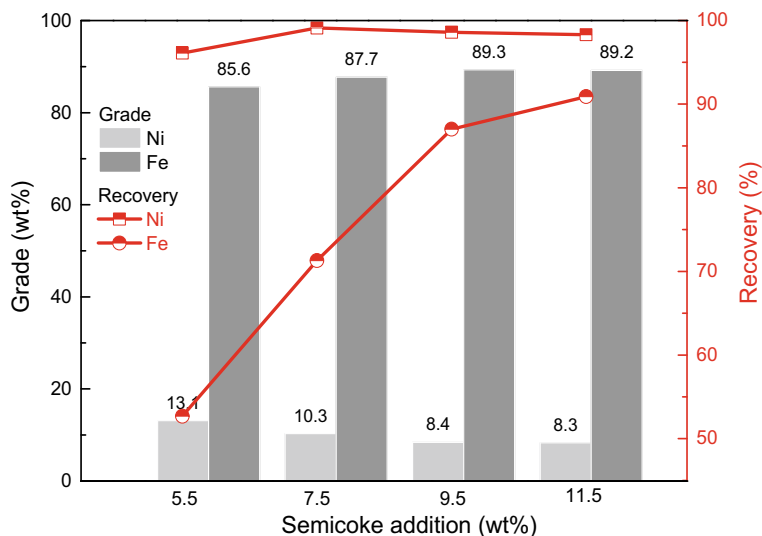


Fig. 3.42 Effect of coke addition on the indexes of ferronickel smelting by fixing smelting temperature of 1500 °C and time of 30 min

In the pre-reduction calcine obtained with different semicoke additions, quicklime was used to adjust the quaternary basicity of the mixture to 0.8 for smelting. The quaternary basicity of slag was 0.74, due to the use of corundum crucible. Figure 3.42 shows the effect of semicoke addition on the grades and recoveries of nickel and iron in ferronickel. With the increase of semicoke amount, the nickel grade in ferronickel decreased gradually and the iron grade increased. With the proportion of semicoke of 5.5 wt%, the contents of nickel and iron in ferronickel were 13.1 wt% and 85.6 wt%, respectively. The recoveries of nickel and iron were 96.1% and 52.7%, respectively. The results showed that the reduction of nickel oxide in laterite ore was sufficient, but the reduction degree of iron oxide was low.

With the increase of the semicoke addition, the reduction of iron oxide in laterite ore was strengthened (Table 3.25). As a result, the iron content in ferronickel increased and the grade of nickel decreased gradually. At this moment, the iron recovery in ferronickel increased, while the nickel recovery was basically constant. With the semicoke addition of 7.5 wt%, the nickel and iron grades in ferronickel were 10.3 wt% and 87.7 wt%, respectively, and the recoveries were 99.1% and 71.3%, respectively. When the semicoke increased to 11.5 wt%, the grades and recoveries of nickel and iron decreased slightly. It might be caused by the reduction of some metal oxides, such as chromium oxide, which formed alloy when excessive semicoke was added.

Table 3.25 Variation of FeO content in slag after adding different amounts of simecoke

Simecoke addition (wt%)	5.5	7.5	9.5	11.5
FeO content (wt%)	13.5	7.6	3.3	2.8

3.5.2 Effect of Quaternary Basicity of Slag

Figure 3.43 shows the indexes of ferronickel smelting with different quaternary basicities. With the increase of the quaternary basicity of slag, the grade and recovery of nickel in ferronickel fluctuated. At the quaternary basicity of 0.65, the grade of nickel in ferronickel was 9.6 wt% and its recovery was 95.9%. As the quaternary basicity reached 0.74, the grade and recovery of nickel increased to 10.3 wt% and 99%, respectively. As the quaternary basicity further increased, the grade of nickel decreased slightly due to the reduction of iron oxide. Considering the grade and recovery of nickel in ferronickel, it was suitable to control the quaternary basicity of slag in the range 0.74–0.78.

Under the given ternary basicity of slag [$R_3 = m(\text{CaO} + \text{MgO})/m(\text{SiO}_2)$], the influence of Al_2O_3 content in slag on the grades and recoveries of nickel and iron in the ferronickel is shown in Fig. 3.44. With the increase of Al_2O_3 content in slag from 6.5 wt% to 9.4 wt%, the grades and recoveries of nickel and iron improved. The nickel grade and its recovery increased from 10.0 wt% to 10.1 wt% and from 93.1% to 93.9% respectively, which indicated that increasing Al_2O_3 content in slag was beneficial to ferronickel smelting. The content of Al_2O_3 in slag increased continuously

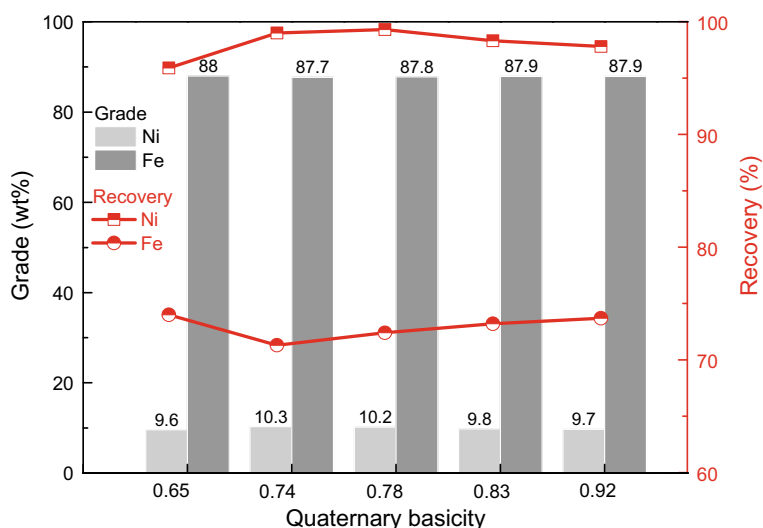


Fig. 3.43 Effect of quaternary basicity on the indexes of ferronickel smelting by fixing semicoke addition of 7.5 wt%, smelting temperature of 1500 °C and time of 30 min

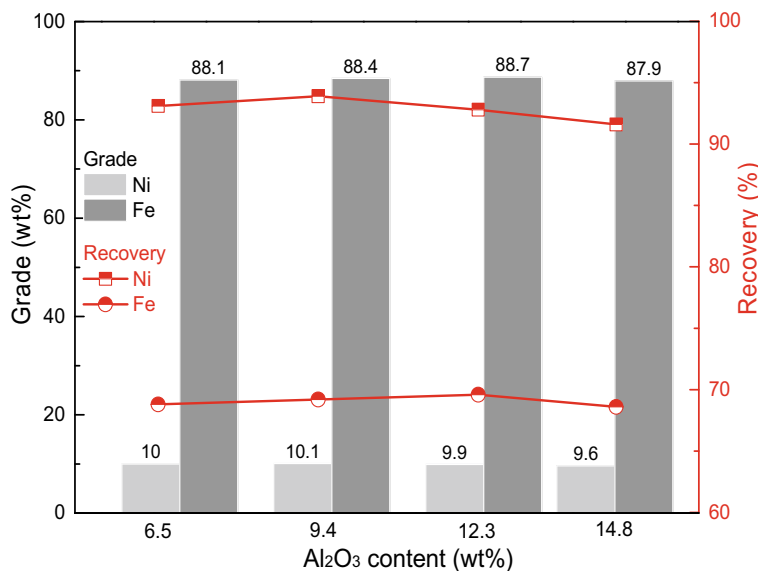


Fig. 3.44 Effect of Al_2O_3 content on the indexes of ferronickel smelting by fixing semicoke addition of 7.5 wt%, smelting temperature of 1500 °C and time of 30 min

and the grade and recovery of nickel decreased. When the Al_2O_3 content increased to 14.8 wt%, the grade and recovery of nickel decreased to 9.6 wt% and 91.6%, respectively.

Figure 3.45 shows the XRD results of slag with different quaternary basicities. At the quaternary basicities of 0.65 and 0.68, the main phases of slag were forsterite and enstatite, causing the poor fluidity of slag. When the quaternary basicity of the slag increased to 0.74, the phase changed obviously, forming a low melting point eutectic composed of diopside and olivine. As a result, the melting temperature of slag decreased and the fluidity of slag improved. In addition, the mass transfer of the ferronickel grains in the slag was more sufficient and the loss of inclusions was reduced, leading to the increase of the grade and recovery of nickel. As the quaternary basicity increased further, the amount of slag increased significantly, which resulted in the increase of inclusion and dissolution loss of nickel.

Figure 3.46 shows the XRD patterns of slag with different Al_2O_3 contents. With increasing Al_2O_3 content from 6.5 to 9.4 wt%, the amounts of forsterite and pyroxene with high melting point obviously decreased and the diopside amount increased. The results showed that the increase of Al_2O_3 content in slag could promote the formation of liquid phase at the relatively low temperature of 1450 °C, improving the fluidity of slag and the grade and recovery of ferronickel. When the Al_2O_3 content in the slag further increased to 12.3 wt%, the magnesium aluminate spinel with high melting point appeared, which led to the increase of the melting temperature of slag. When the Al_2O_3 content in the slag was more than 9.4 wt%, the smelting conditions would be worsen, leading to the decreases of nickel grade and recovery in ferronickel.

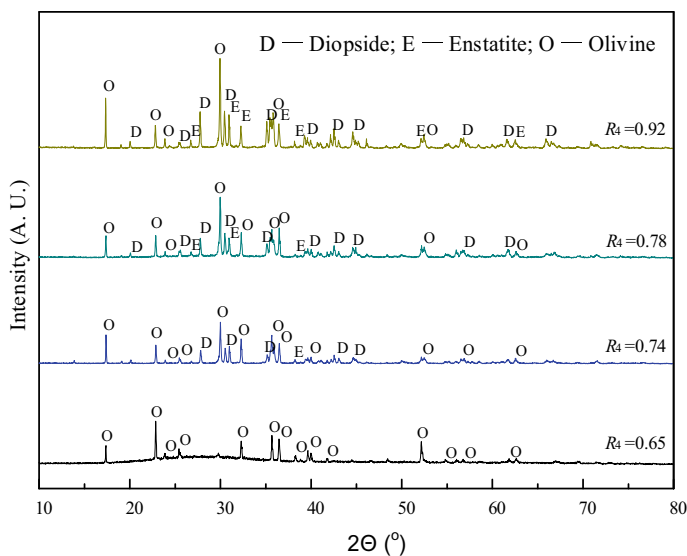


Fig. 3.45 XRD patterns of slags with different quaternary basicities by fixing semicoke addition of 7.5 wt%, smelting temperature of 1500 °C and time of 30 min

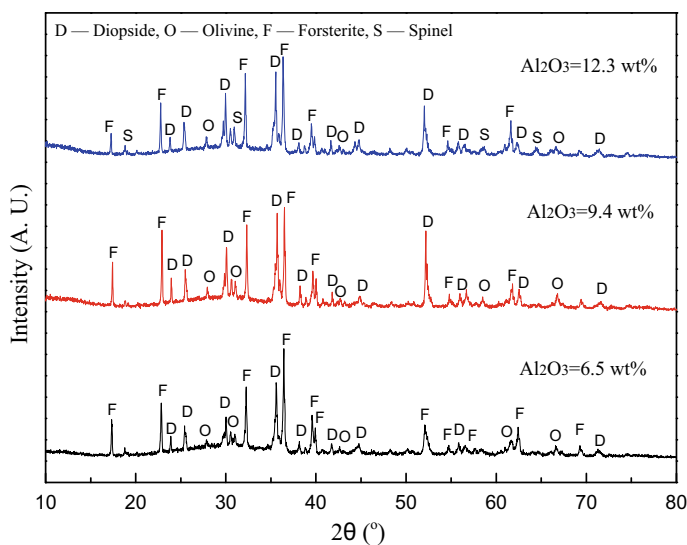


Fig. 3.46 XRD patterns of slags with different Al_2O_3 contents by fixing semicoke addition of 7.5 wt%, smelting temperature of 1450 °C and time of 30 min

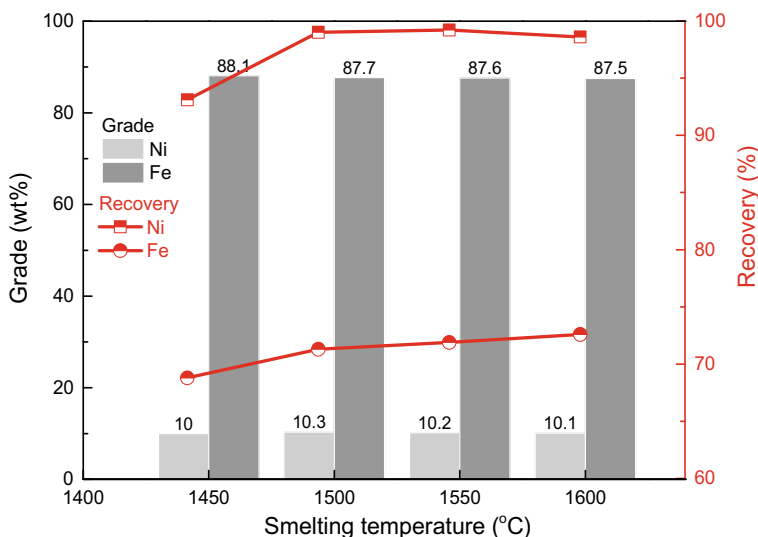


Fig. 3.47 Effect of smelting temperature on the indexes of ferronickel smelting by fixing semicoke addition of 7.5 wt%, quaternary basicity of 0.74 and smelting time of 30 min

3.5.3 Effect of Smelting Temperature

Figure 3.47 shows the effect of smelting temperature on the grades and recoveries of nickel and iron in ferronickel. The proper increase of smelting temperature is beneficial to the grade and recovery of nickel. When the smelting temperature increased from 1450 °C to 1500 °C, the grade and recovery of nickel increased from 10 wt% to 10.3 wt% and from 93.1 % to 99%, respectively. The further increase in the smelting temperature had no obvious effect on the grade and recovery of nickel. The results showed that the fluidity of the slag could be guaranteed at 1500 °C with the suitable quaternary basicity of slag to facilitate separation of ferronickel from slag.

3.5.4 Effect of Smelting Time

The effects of smelting time on the grades and recoveries of nickel and iron in ferronickel are shown in Fig. 3.48. With the prolongation of smelting time, the grades of nickel and iron in ferronickel decreased slightly, while the recoveries of nickel and iron showed the increasing trend with increasing smelting time. When the smelting time increased from 20 to 30 min, the recovery of nickel in ferronickel increased from 97.2 % to 99% and the recovery of iron increased from 68.7 % to 71.7 %.

Above all, the laboratory scale tests showed that under the suitable conditions of semicoke addition of 7.5 wt%, reductive roasting temperature of 950 °C, reductive

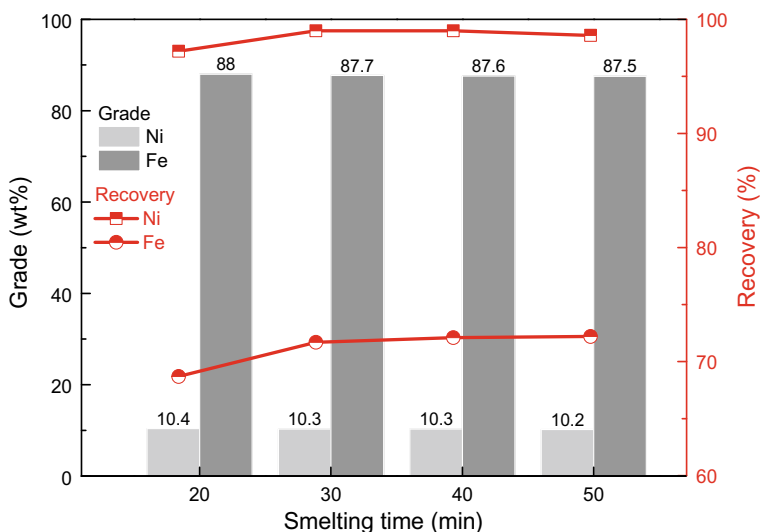


Fig. 3.48 Effect of smelting time on the indexes of ferronickel smelting by fixing semicoke addition of 7.5 wt%, quaternary basicity of 0.74 and smelting temperature of 1500 °C

Table 3.26 Suitable chemical composition of smelting slag (wt%)

FeO	CaO	MgO	Al ₂ O ₃	SiO ₂	Quaternary basicity
7.6	15.9	21.9	7.1	43.9	0.74

roasting time of 120 min, smelting temperature of 1500 °C, smelting time of 30 min and quaternary basicity of 0.74 (Table 3.26), the ferronickel with the nickel and iron grades of 10.3 wt% and 87.7 wt% could be prepared from a saprolitic laterite ore with the nickel and iron contents of 1.9 wt% and 22.1 wt%, respectively, and the recovery percentage of nickel in ferronickel reached 99%.

3.6 Pilot-Scale Tests

3.6.1 Raw Materials

The materials used in the pilot-scale tests included laterite ore, bitumite, semicoke and limestone.

Table 3.27 Main chemical compositions of laterite ores used in pilot-scale tests (wt%)

Laterite ore	Fe _{total}	Ni	SiO ₂	MgO	Al ₂ O ₃	CaO	LOI*
B	20.6	1.7	34.8	12.1	2.8	1.5	11.2
C	47.8	0.8	3.5	1.5	7.1	1.5	13.4

LOI Loss on ignition

3.6.1.1 Laterite Ore

Laterite ore-B and laterite ore-C were used for the pilot-scale smelting tests. The main chemical compositions of the laterite ores are shown in Table 3.27. Laterite ore-B was a typical saprolitic laterite ore. Its nickel content was 1.7 wt% and total iron content was 20.6 wt%. Besides, the contents of MgO, SiO₂ and Al₂O₃ reached 12.1 wt%, 34.8 wt%, and 2.8 wt%, respectively. Laterite ore-C was a typical limonitic laterite ore, characterized by high Fe and Al₂O₃ contents, as well as low Ni, SiO₂, and MgO contents. The contents of nickel and total iron in the laterite ore-C were 0.8 wt% and 47.8 wt%, respectively. The contents of MgO, SiO₂ and Al₂O₃ were 1.5 wt%, 3.5 wt%, and 7.1 wt%, respectively.

Laterite ore-B and Laterite ore-C were mixed with a mass ratio of 1:1. The grades of nickel and iron in the mixed ore were 1.3 wt% and 34.2 wt% respectively, and the mass ratio of iron to nickel was close to 28. The contents of CaO, MgO, Al₂O₃ and SiO₂ in the mixed ore were 1.5 wt%, 6.8 wt%, 4.9 wt% and 19.3 wt%, respectively. The MgO/SiO₂ mass ratio and quaternary basicity were 0.35 and 0.34, respectively.

3.6.1.2 Bitumite

Bitumite- A was used to provide heat during drying and pre-reduction of laterite ore and it was also used as reducing agent in rotary kiln. The particle size of bitumite was 20–40 mm. The results of proximate analysis are shown in Table 3.28 and the main chemical composition of its ash is shown in Table 3.29. The fixed carbon content of bitumite was 49.8 wt% and the volatile matter content was 33.3 wt%. The ash content was 13.8 wt%. The softening temperature of ash was 1220 °C. Besides, the calorific value of bitumite-A was 28.3 kJ/kg.

Table 3.28 Proximate analysis of bitumite-A and ash fusion characteristics

Proximate analysis (wt%)				Ash fusion characteristics (°C)		
M _{ad}	A _d	V _{daf}	F _{Cad}	ST	HT	FT
3.1	13.8	33.3	49.8	1220	1250	1270

F_{Cad}: Fixed carbon content; V_{daf}: volatile matter content; A_d: Ash content; M_{ad}: Moisture; ST: Softening temperature; HT: Hemispherical fusion temperature; FT: Flow temperature

Table 3.29 Main chemical composition of bitumite-A ash (wt%)

Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	MgO
9.1	57.5	18.0	2.1	1.1	2.0

Table 3.30 Proximate analysis of semicoke-B and ash fusion characteristics

Proximate analysis (wt%)				Ash fusion characteristics (°C)		
M _{ad}	A _d	V _{daf}	F _{Cad}	ST	HT	FT
5.46	9.48	4.33	80.73	1120	1140	1170

Table 3.31 Main chemical composition of semicoke-B ash (wt%)

Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	MgO
8.7	54.0	14.7	10.7	0.8	1.8

3.6.1.3 Semicoke

Semicoke-B was mainly used for reduction of nickel and iron oxides in the smelting of laterite ore. The particle size of semicoke-B was 20–40 mm. Table 3.30 shows the proximate analysis of semicoke-B and its ash fusion characteristics. Table 3.31 shows the chemical composition of its ash. The fixed carbon content of semicoke was 80.7 wt% and the volatile matter content was 4.3 wt%. Moreover, the ash content was 9.5 wt%. The characteristic fusion temperature of ash was relatively low, namely 1170 °C.

3.6.1.4 Quick Lime

Quick lime-A with particle size of 20–40 mm was used to adjust the quaternary basicity of smelting slag. Table 3.32 shows the main chemical composition of quick lime-A. It shows that its CaO content was 86.8 wt%.

Table 3.32 Main chemical composition of quick lime-A (wt%)

CaO	TFe	MgO	SiO ₂	Al ₂ O ₃
86.8	0.1	4.1	2.9	0.05

3.6.2 Experimental Procedure

The typical RKEF process was adopted in the pilot-scale tests, including drying of laterite ore, reductive roasting and electric furnace smelting. The flowsheet of the pilot-scale tests is shown in Fig. 3.49 and the main apparatuses are shown in Fig. 3.50.

The procedure was as follows:

- (1) Laterite ore-B and laterite ore-C were mixed with a mass ratio of 1:1 and the mixture was dried in a rotary dryer with a diameter of 1 m and a length of 10 m. Hot air was introduced into the head of the rotary dryer to dry the wet ore in the form of downstream flow. The drying temperature was 800–850 °C and the discharging temperature was lower than 90 °C.
- (2) After the dried ore was mixed with a certain proportion of semicoke, it was charged into a rotary kiln for reductive roasting. The rotary kiln had a diameter of 1.5 m and a length of 12.5 m. In the kiln, the pre-reduction temperature was 800–950 °C. The maximum temperature was not more than 1000 °C and the reduction time was 1–2 h. The amount of semicoke was 8.5–13.5 wt% and the feeding speed at the kiln tail was 800–1000 kg/h. The fuel of rotary dryer and rotary kiln was pulverized bitumite provided by a coal mill and it was directly supplied to kiln through blowing. The amount of injected pulverized coal was about 12–15 wt%.

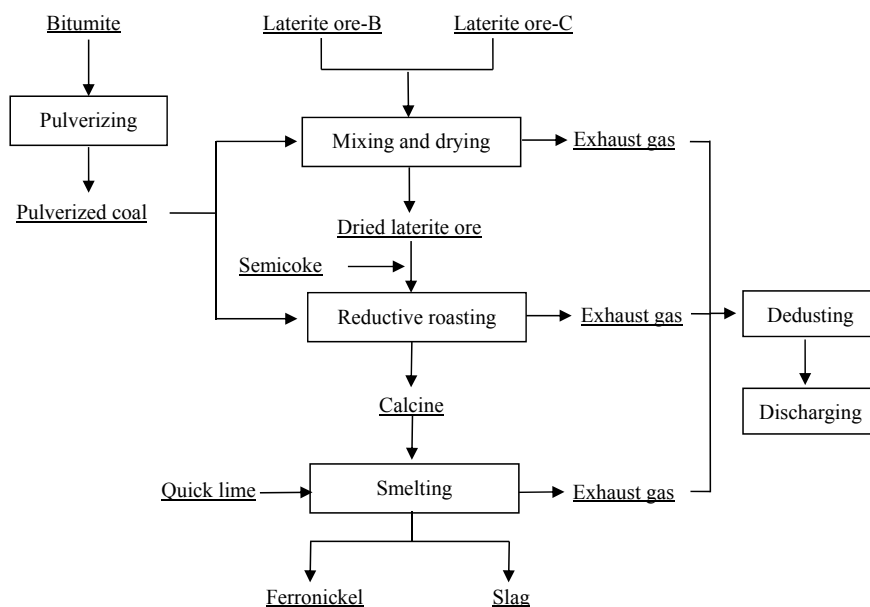


Fig. 3.49 Flowsheet of ferronickel-making in the pilot-scale tests

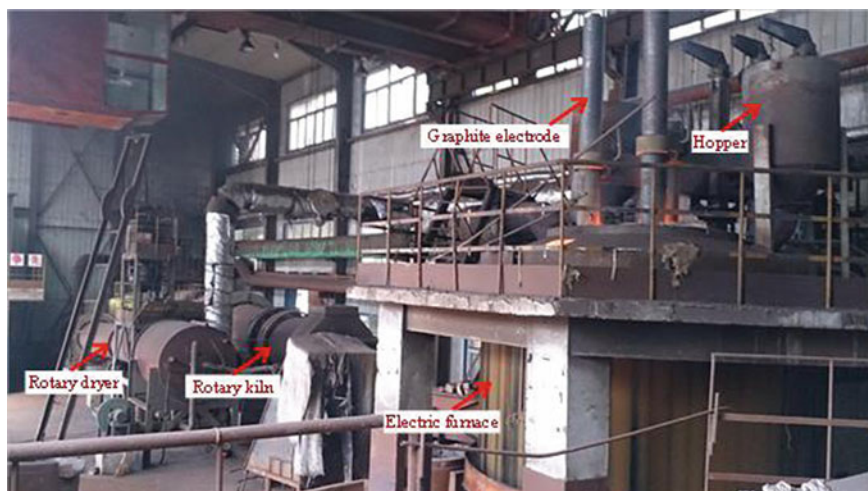


Fig. 3.50 Main apparatuses of the pilot-scale tests (Owned by CNMC Shengyang Research Institute of Nonferrous Metals Co. Ltd.)

- (3) After reductive roasting, the hot calcine was loaded into a hopper and its temperature was kept at 500–700 °C. After adding quick lime in a certain proportion based on the given quaternary basicity, the feed was charged into the electric furnace with an inner diameter of 2.5 m and a height of 2.5 m. The furnace was equipped with three graphite electrodes with a diameter of 1.0 m. After smelting at 1550 °C for 4–6 h, the molten ferronickel and slag were discharged simultaneously. The pilot-scale tests were continuously operated for 16 days, consuming 210 t of laterite ore.
- (4) The exhaust gas produced from rotary dryer, rotary kiln and electric furnace was discharged after dedusting.

3.6.3 Results and Discussion

The effects of the quaternary basicity on the separation of slag and ferronickel were evaluated by conducting pilot-scale tests. Table 3.33 lists the main chemical compositions of the slags and Table 3.34 lists main compositions of ferronickel.

By adding quick lime to adjust the quaternary basicity of slag, the fluidity of slag could be significantly improved and the electrode could be lowered smoothly, which was favorable for the subsequent separation of slag and iron. According to the results in Tables 3.33 and 3.34, it was appropriate to adjust the quaternary basicity of slag to about 0.60–0.68, which was consistent with the previous theoretical analyses. At the quaternary basicity below 0.55 (Test 1 and Test 2), the content of nickel in the slag was relatively high. For example, the content of nickel in the slag was as high as 0.28 wt% at quaternary basicity of 0.55. A low nickel recovery (80–85%) was estimated from ferronickel. However, at quaternary basicity of 0.60–0.66, the content

Table 3.33 Main compositions of slags in the pilot-scale tests (wt%)

No.	TFe	FeO	TNi	MgO/SiO ₂ mass ratio	Quaternary basicity R_4
1	7.1	6.6	0.10	0.30	0.29
2	9.9	9.5	0.28	0.39	0.55
3	22.7	26.8	0.039	0.44	0.68
4	28.3	33.4	0.075	0.38	0.63
5	4.5	5.4	0.014	0.40	0.60
6	7.6	9.2	0.008	0.41	0.66
7	9.8	12.3	0.069	0.38	0.60

Table 3.34 Main compositions of ferronickel in the pilot-scale tests (wt%)

No.	C	Cr	TNi	TFe	S	P
1	1.74	0.51	3.42	92.20	0.97	0.217
2	1.22	0.234	3.82	93.70	0.56	0.020
3	0.028	0.042	4.88	94.10	0.307	0.081
4	0.045	0.053	5.35	93.80	0.151	0.017
5	1.81	1.37	3.50	92.50	0.306	0.055
6	1.93	2.54	3.25	90.40	0.268	0.037
7	1.97	1.51	3.15	92.7	0.233	0.054

of nickel in the smelting slag decreased obviously. The nickel contents in the slag were only 0.008 wt% at quaternary basicity of 0.66, resulting in a nickel recovery of 99%. These results indicated that increasing the quaternary basicity would be beneficial for the recovery of nickel at the constant smelting temperature owing to the decreased viscosity of slag. As shown in Table 3.34, the nickel grades of Test 3 and Test 4 were higher than other results, due to the relatively small amount of semicoke addition. More iron oxides were not reduced to metallic iron and remained in the slag (Table 3.33), resulting in the reduction of content of metallic iron in ferronickel and the increase of nickel grade.

Figures 3.51 and 3.52 show the external morphologies of the air-cooled smelting products. When the quaternary basicity was 0.55, the tight integration between the slag and ferronickel resulted in an inefficient separation (Fig. 3.51) due to high viscosity. During the cooling process, the semicoke particles remained in the surface of ferronickel, thus affecting the production and quality of ferronickel. Evidently, a higher smelting temperature was necessary under the current conditions. Nevertheless, when the quaternary basicity was 0.66, the slag and ferronickel were completely separated (Fig. 3.52), indicating that the current smelting temperature was sufficient. The fluidity of molten iron and the separation of slag and iron could be improved after slag formation control. As a result, the feasibility of controlling the slag formation to decrease the smelting temperature was verified.

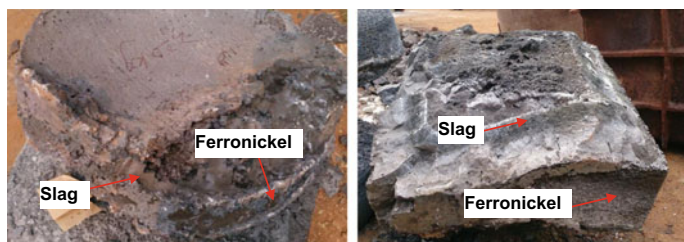


Fig. 3.51 External morphology of air-cooled smelting products in the pilot-scale test (quaternary basicity of 0.55), reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

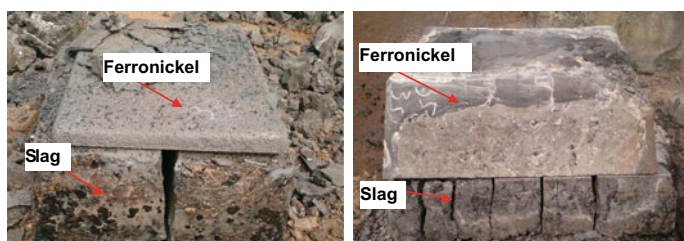


Fig. 3.52 External morphology of air-cooled smelting products in the pilot-scale test (quaternary basicity of 0.66), reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

3.7 Industrial Applications

Controlling the slag formation can help decrease the melting temperature of slag. However, the addition of lime increases the amount of slag output, resulting in higher energy consumption to maintain the slag temperature during smelting. The industrial tests were carried out to determine the suitable oxides dosages and smelting temperature.

3.7.1 Industry Practice in Plant-A

The industrial tests were performed in plant-A, which had four RKEF production lines. The diameter and length of the rotary dryer were 4 m and 70 m, respectively. The diameter and length of rotary kiln were 4.4 m and 110 m, respectively. The transformer capacity of the electric furnace was 33,000 kVA. Three types of dried laterite ores (laterite ores-D, E, and F) were mixed with certain mass proportions. The MgO/SiO_2 mass ratio was fixed at 0.63. Bitumite-B was pulverized before injecting it into the kiln for burning. Semicoke (4–6%) and other additives (such as calcined lime and bitumite lump, if necessary) were then added to the mixture, which was reduced in the temperature range 750–800 °C in the rotary kiln for 2 h. The hot feeds

Table 3.35 Main chemical compositions of laterite ores used in the industrial tests (wt%)

Laterite ore	Fe _{total}	Ni	SiO ₂	MgO	Al ₂ O ₃	CaO	LOI*
D	15.8	1.3	35.7	26.2	1.9	0.2	10.7
E	16.7	1.9	42.4	18.1	3.0	0.7	10.3
F	25.1	1.5	24.3	18.8	1.6	0.1	12.1

*LOI Loss on ignition

Table 3.36 Proximate analysis of bitumite-B and its ash compositions (wt%)

Proximate analysis*				Main chemical composition of ash				
F _{cad}	V _{daf}	A _d	M _{ad}	TFe	SiO ₂	CaO	Al ₂ O ₃	MgO
57.6	31.1	10.4	0.9	15.9	40.1	13.4	20.3	2.2

*F_{cad}: Fixed carbon content; V_{daf}: volatile matter content; A_d: Ash content; M_{ad}: Moisture content

Table 3.37 Proximate analysis of semicoke-C and its ash compositions (wt%)

Proximate analysis				Chemical composition of ash				
F _{Cad}	V _{daf}	A _d	M _{ad}	TFe	SiO ₂	CaO	Al ₂ O ₃	MgO
86.0	6.4	6.8	0.8	10.2	46.2	15.8	9.5	4.2

Table 3.38 Main chemical composition of quick lime-B (wt%)

CaO	TFe	MgO	SiO ₂	Al ₂ O ₃
92.3	0.1	2.0	0.4	0.02

were continuously charged into the electric furnace. After smelting for 4–5 h, the molten ferronickel and slag were discharged, respectively.

Table 3.35 lists the main chemical compositions of laterite ores. Tables 3.36 and 3.37 show the proximate analyses of bitumite-B and semicoke-C, respectively. Table 3.38 lists the chemical composition of quick lime-B. It should be noted that the industrial practices lasted for more than two years. The compositions of laterite ores had some changes in this period because they were obtained from different suppliers.

3.7.1.1 Regulation of FeO Content in the Final Slag

Test 1 provided the results before slag control and its slag with the quaternary basicity of 0.58 and FeO content of 5.0 wt% required a high smelting temperature of 1601 °C (Table 3.39). This temperature could be lowered by nearly 50 °C by regulating the FeO content to 9.9 wt% (Test 2), thus decreasing the energy consumption from 3820 kW·h/t-ferronickel to 3430 kW·h/t-ferronickel (Table 3.40). The increase in the FeO content led to a decrease in the flow temperature (Table 3.41) and viscosity

Table 3.39 Variation of smelting temperature after slag control applied in Plant-A

Test	Slag control			Smelting temperature (°C)
	FeO content (wt%)	MgO/SiO ₂ mass ratio	Quaternary basicity R_4	
1	5.0	0.62	0.58	1601
2	9.9	0.65	0.62	1552
3	9.6	0.65	0.65	1548
4	6.8	0.63	0.67	1565
5	12.5	0.63	0.61	1515
6	11.0	0.64	0.63	1575

Table 3.40 Main smelting indexes after slag control

Test	Average energy consumption (kW·h/t-ferronickel)	Quick lime dosage (Kg/t-ferronickel)
1	3820	0
2	3430	0
3	3370	140–160
4	3160	260–300
5	3100	0
6	3220	0

Table 3.41 Flow temperatures of smelting slags measured in an inert atmosphere

Test No.	1	2	3	4	5	6
Flow temperature (°C)	1415	1390	1385	1345	1365	1360

of slag (Fig. 3.53). Consequently, the smelting temperature and energy consumption decreased.

3.7.1.2 Regulation of Quaternary Basicity

Under the same conditions as those in Test 2, an additional amount of lime (140–160 kg/t-ferronickel) was added to adjust the quaternary basicity of slag from 0.62 to 0.65 (Test 3). Consequently, the consumption of laterite ore increased from 18,258 tons to 19,135 tons within the same period (Fig. 3.54). This was because the decreased melting temperature (Table 3.41) accelerated melting of the pre-reduced feeds. The smelting temperature and the total energy consumption showed no evident change (Table 3.39 and Fig. 3.54) and the increase of ferronickel output from 2053 tons to 2112 tons indicated a decrease of average energy consumption from 3430 kW·h/t-ferronickel to 3370 kW·h/t-ferronickel.

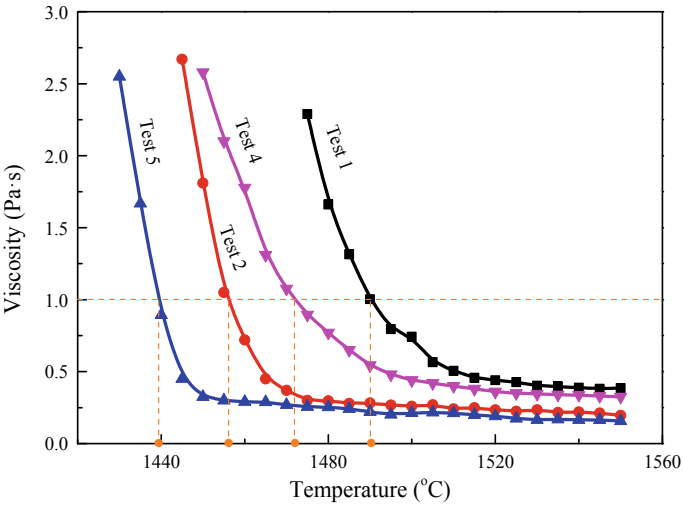


Fig. 3.53 Variation of the viscosity of slag with temperature

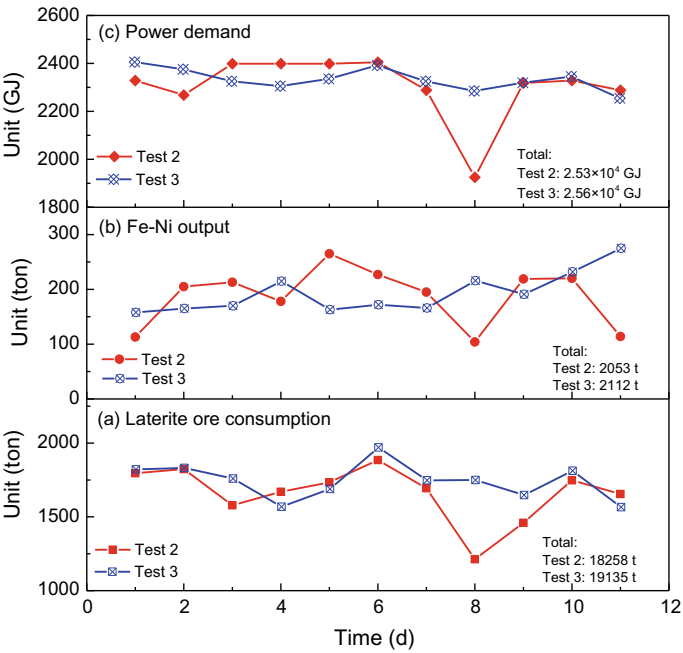


Fig. 3.54 Laterite ore consumption, ferronickel output, and energy consumption per day, reprinted from Ref. [8], copyright 2022, with permission from Elsevier Ltd

Table 3.42 FeO contents in the laterite ore after rotary kiln roasting

Test	1	2	3	4	5	6
FeO content (wt%)	~10	~10	~10	~18	~18	~18

3.7.1.3 Combined Regulation of FeO Content and Quaternary Basicity

The quaternary basicity and FeO content of the preliminary (pre-reduced) slag and final slag were simultaneously regulated. 2 wt% of bitumite-B (particle size: 20–40 mm) was added to the kiln to increase the FeO content of the reduced feeds. The FeO content in the reduced feeds increased from 10 wt% to approximately 18 wt% (Table 3.42). Moreover, an additional amount of lime (260–300 kg/t-ferronickel) was added to adjust the quaternary basicity to 0.67 (Test 4). Due to the low FeO content of 6.8 wt% (Table 3.39), the viscosity of slag was higher than that in Test 2 (Fig. 3.53), causing its higher smelting temperature. However, the flow temperature of slag was lowered to 1345 °C (Table 3.41). The decrease in the energy consumption depended more on shortening the smelting time by fast melting of the feeds.

Compared with Test 4, Test 5 was conducted with a higher FeO content and lower quaternary basicity. The smelting temperature decreased from 1565 °C to 1515 °C (Table 3.39), due to the lower viscosity (Fig. 3.53). A remarkable decrease of 37 °C in the smelting temperature relative to Test 2 was achieved by increasing the FeO content in the slag. The drop in the smelting temperature reached 86 °C, by comparing Tests 1 and 5. Furthermore, the average energy consumption for ferronickel was lowered to 3100 kW·h/t (Table 3.40), a decrease of 720 kW·h/t-ferronickel compared with that of Test 1.

It should be noted that the high FeO content in the final slag indicated that more iron was discharged into the slag, leading to a lower iron recovery in ferronickel. The energy consumption decreased from 3160 kW·h/t-ferronickel in Test 4 to 3100 kW·h/t in Test 5. However, the iron recovery in Test 4 was increased by approximately 10% compared with that in Test 5. In other words, to obtain high recovery of iron, the quaternary basicity could be increased appropriately. Conversely, a high FeO content and a low quaternary basicity of the slag would be preferred.

The low silicon and chromium contents of ferronickel (Si: 0.06 wt%; Cr: 0.76 wt%; Test 3, as shown in Table 3.43) were obtained in Tests 1 to 3. In order to recover chromium from laterite ores and to produce the high chromium-containing ferronickel, the industrial tests were further carried out. Compared with the production of low-chromium ferronickel, increasing the chromium content required higher smelting temperature due to the high reduction temperature of chromium oxide. As shown in Test 6, when the chromium content in ferronickel was 1.48 wt% (Table 3.43), the smelting temperature reached 1575 °C (Table 3.39). When the quaternary basicity increased from 0.63 to 0.67, the chromium content increased to 2.78 wt% at the smelting temperature of 1565 °C. These results showed that controlling slag formation was also helpful to enhancement of the grade and recovery of chromium in ferronickel. Meanwhile, the average energy consumption of ferronickel decreased

Table 3.43 Contents of carbon, chromium and silicon in ferronickel (wt%)

Tests	C	Cr	Si
3	2.45	0.76	0.06
4	2.57	2.78	2.33
6	2.19	1.48	2.34

from 3220 kW·h/t to 3160 kW·h/t (Tests 4 and 6 in Table 3.40). Increasing the quaternary basicity was also conducive to reduction of the FeO content in slag. Compared with Test 6, the FeO grade of slag in Test 4 was reduced by 3 wt% and the recovery of iron in ferronickel was increased by 5–10%.

3.7.2 Industry Practice in Plant-B

The industrial tests were further performed in Plant-B, which had two RKEF production lines. The transformer capacity of electric furnace was 25,500 kVA. Table 3.44 shows the variation of smelting temperature and average energy consumption after slag control. Test 1 provided the results before slag control and its slag with quaternary basicity of 0.53 and FeO content of 9.9 wt% required a smelting temperature of 1587 °C and average energy consumption of 4100 kW·h/t-ferronickel. After controlling the quaternary basicity of 0.70 and FeO content of 3.4 wt% in the slag, the smelting temperature lowered to 1570 °C, thus decreasing the energy consumption to 3635 kW·h/t-ferronickel, indicating a decrease of 11%. With the further control of quaternary basicity of 0.63 and FeO content of 6.4 wt%, respectively, the smelting temperature was further reduced to 1545 °C. The energy consumption of electric furnace smelting was only about 3500 kW·h/t-ferronickel, which was reduced by 600 kW·h/t-ferronickel compared with Test 1.

The long-term practices showed that the technology of controlling slag formation can be applied to the ferronickel plants in different scales of electric furnaces and the adaptability of raw laterite ores is also strong. The new technology has the potential to significantly reduce the energy consumption of electric furnace smelting, lowering the cost of ferronickel production.

Table 3.44 Variation of smelting temperature and energy consumption after slag control applied in Plant-B

Test	Slag control			Smelting temperature (°C)	Average energy consumption (kW·h/t-ferronickel)
	FeO content (wt%)	MgO/SiO ₂ mass ratio	Quaternary basicity R_4		
1	9.9	0.49	0.53	1587	4100
2	3.5	0.60	0.70	1570	3635
3	6.4	0.50	0.63	1545	3500

3.7.3 Assessment of Energy Conservation and Emission Reduction

After the industrial test, the slag control technique was continuously applied to Plant-A. The quaternary basicity was maintained in the range 0.65–0.67, and the FeO contents were in the ranges 16–20 wt% and 6–8 wt% in the preliminary and final slag, respectively. The energy consumptions before and after applying the new method were compared. It should be noted that the ferronickel output in the plant was affected by a combination of factors, such as the laterite ore sources (supplied from different areas in Indonesia or Philippines), the equipment shutdown and overhaul.

Table 3.45 shows that the energy consumption decreased from 865 million kW·h before slag control to 805 million kW·h per year after slag control, with a slight decrease of ferronickel output from 0.244 to 0.24 million tons. The average energy consumption decreased from 3541 h/t-ferronickel to 3355 kW·h/t-ferronickel, i.e., a decline of 5.3%. The long-period practice further confirmed the effectiveness of the slag control. With the annual output of 0.24 million tons of ferronickel, the energy consumption could be reduced by 44.45 million kW·h per year in the plant. Based on the emission of 1.01 kg of carbon dioxide per kilowatt-hour in the coal-fired power plants[28,29], it was equivalent to the reduction of carbon dioxide emission by 45 kilotons a year (Table 3.46).

Table 3.45 Ferronickel output and power consumption before and after slag control

Month	Ferronickel output (kilotons)		Energy consumption (Million kW·h)		Average energy consumption (kW·h/t-ferronickel)	
	Before	After	Before	After	Before	After
1	15.63	13.57	58.06	44.45	3713.91	3275.54
2	19.35	27.88	70.01	91.95	3618.07	3298.60
3	20.67	23.50	72.78	78.62	3520.84	3345.27
4	22.19	11.20**	76.95	41.95	3468.33	3745.58
5	21.29	17.75	75.56	51.67	3548.62	2911.34
6	15.16	16.84	55.56	58.06	3665.02	3447.50
7	17.79	22.38	60.01	73.90	3373.60	3302.49
8	23.18	25.92	76.67	90.01	3308.32	3471.39
9	22.79	13.45**	77.78	48.06	3413.61	3573.62
10	21.44	22.32	75.84	71.12	3536.67	3186.92
11	20.37	22.43	78.62	71.67	3859.75	3194.98
12	24.34	22.72	86.95	83.62	3571.95	3680.02
Total	244.20	239.95	864.79	805.06	/	/
Average	/	/	/	/	3541.39	3354.99

** : reduction of ferronickel output due to overhaul

Table 3.46 Energy conservation and emission reduction after slag control

Application target	Ferronickel output (million tons)	Energy conservation (million kW·h)	Emission reduction (million tons-CO ₂)
Plant-A	0.24	44.45	0.045
China and Indonesia	12.00	2233.51	2.25

Since 2019, approximately 12 million tons of ferronickel has been produced in China and Indonesia annually and the electric furnaces used for the production have an average transformer capacity of 33,000–36,000 kVA (similar to that of industrial plant-A). With the application of this technology to plants in China and Indonesia, it is expected to reduce the energy consumption by 2233.51 million kW·h per year and carbon dioxide emissions by 2.25 million tons per year.

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Chapter 4

Softening–Melting Properties of Laterite Ore and Regulation Technology Applied in Krupp–Renn Process and Sintering Process



Abstract Producing a certain amount of liquid phase is crucial for the growth and aggregation of ferronickel particles during reductive roasting of laterite ore in the Krupp–Renn process and for mineralization of the ore during its sintering to enhance the sinter output and quality. In this chapter, the effects of the flux addition, roasting temperature and atmosphere on the phase transformation and softening–melting properties of laterite ore were studied and the correlation between phase transformation and softening–melting properties was ascertained. Thereafter, the corresponding regulation technology of softening–melting performance of laterite ore based on the quaternary basicity control was proposed. The efficiencies of the regulation technology applied in the Krupp–Renn process and sintering process were also verified.

Keywords Fusion property · Quaternary basicity · Ferronickel grain growth · Phase transformation · Diopside · Krupp–Renn process · Sintering

In the rotary kiln direct reduction process, in order to achieve the effective physical separation of ferronickel and non–magnetic residue from reduction product, generation of semi–fused laterite lumps are required during reductive roasting in rotary kiln [1–4], so as to promote the mass transfer and to improve the aggregation and growth of ferronickel particles [5–7]. Besides, laterite ores should be agglomerated via sintering in advance for blast furnace smelting [8, 9]. Hence, a proper amount of liquid phase needs to be produced during sintering to strengthen the mineralization and to improve the quality of sinter [10, 11].

Laterite ores contain the high contents of silicon, magnesium, aluminum and other impurities, which have adverse effects on the softening–melting properties of sinter [12, 13]. During roasting, the silicon and magnesium minerals in laterite ores are transformed into refractory silicate minerals such as pyroxene and forsterite with high melting points [14–16], resulting in a series of problems, such as high reductive roasting temperature required in the direct reductive process [4, 17, 18] and unsatisfied sinter yield and quality in the sintering process [11, 19, 20].

To solve these problems in the direct reduction process and the sintering process, it is necessary to determine the phase transformation of laterite ore during roasting and its influencing factors [7, 21, 22] and then establish the relationship between the

phase transformation and softening–melting performance and to determine suitable low melting phase and its formation conditions in the roasting process [23, 24]. The softening–melting properties of laterite ore can be regulated through limiting the formation of high melting point phases and obtaining the suitable low melting point phases [12, 13]. As a result, the formation temperature of liquid phase of laterite ore can be reduced, which enhances the growth of ferronickel particles in the direct reduction process and improves the quality of sinter in sintering process.

4.1 Phase Transformation of Laterite Ore During Roasting

4.1.1 Experimental

The typical saprolitic laterite ore was taken from Sulawesi Island, Indonesia. The sample was dried at 110 °C for 2 h and then ground to 100% of the particles passing through a 0.1 mm–pore size sieve. The chemical composition of the sample is shown in Table 4.1. It was characterized by high magnesia and silica contents. The contents of total iron and nickel were 22.1% and 1.91%, respectively. According to the XRD results, the laterite ore mainly consisted of lizardite ($(\text{Mg, Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$), goethite and hematite (Fig. 4.1).

The mixture of laterite ore and CaO of analytic grade was briquetted into cylindrical briquettes (4.0 g, diameter of 10 mm and height of 15 mm) at the pressure of 5 MPa, which were dried at 110 °C for 4 h subsequently. The dried briquettes were loaded into a corundum crucible and roasted in a reductive atmosphere with given CO partial fractions for 1 h with the roasting temperature varying from 1100 °C to 1300 °C. The schematic diagram of the horizontal tube furnace is shown in Fig. 4.2. In all cases, the gas flow rate was 350 L/h. After roasting, the furnace was shut down and the gas was shifted from CO to N₂ (99.99% purity). The crucible was moved to the low–temperature zone of the tube and the system was cooled to room temperature with a cooling speed of 40 °C/min. A part of reduced briquettes were prepared for XRD analysis and another part of the briquettes were mounted into an epoxy resin mould, ground and polished to prepare cross–sections for microstructure observation.

Table 4.1 Chemical composition of saprolitic laterite ore (wt%)

Composition	Fe _{total}	Ni	SiO ₂	MgO	Al ₂ O ₃	CaO	Cr ₂ O ₃	LOI*
Content	22.1	1.9	26.5	13.4	4.3	2.0	1.7	13.2

*LOI is mass loss on ignition

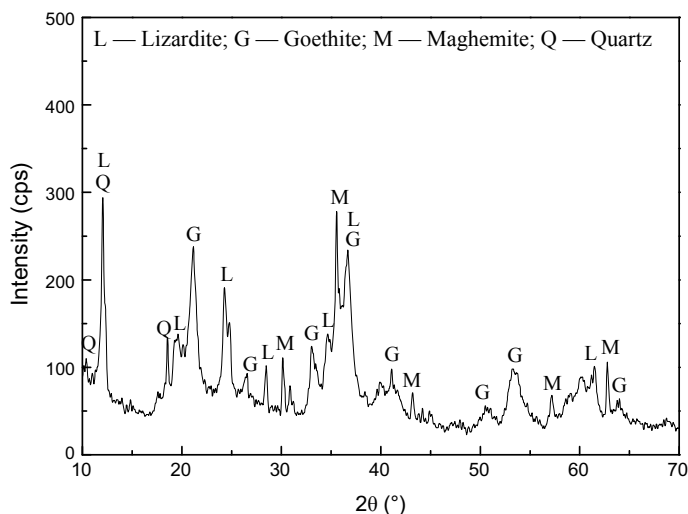


Fig. 4.1 XRD pattern of the saprolitic laterite ore

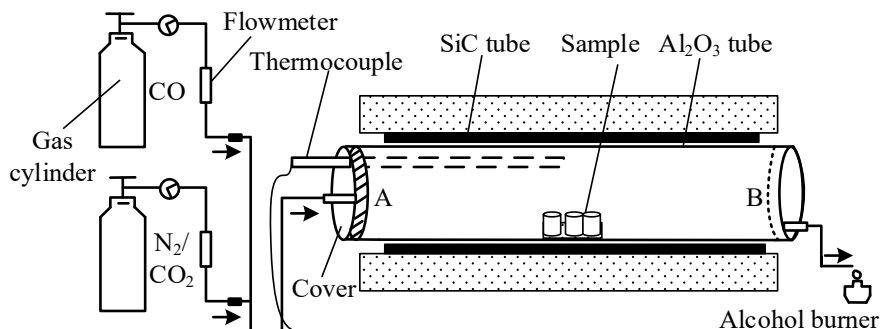


Fig. 4.2 Schematic diagram of the horizontal tube furnace

4.1.2 Effect of CaO Content

The phase transformation of the laterite ore with natural CaO content of 2 wt% roasted at different temperatures for 1 h in air was examined firstly and the results are shown in Fig. 4.3. At the temperature of 800 °C, the major mineral constituents were hematite (Fe_2O_3) and forsterite (Mg_2SiO_4) which were generated from the dehydration of goethite and dehydroxylation of lizardite, respectively. When the roasting temperature increased to 1000–1100 °C, the diffraction peaks of hematite (Fe_2O_3) and forsterite (Mg_2SiO_4) were weakened, along with the appearance of enstatite (MgSiO_3) and spinel (MgFe_2O_4). It indicated that the reaction of hematite and forsterite combined to form spinel and pyroxene in the temperature range 1000–1100 °C. With the further increase in the roasting temperature, the diffraction peaks

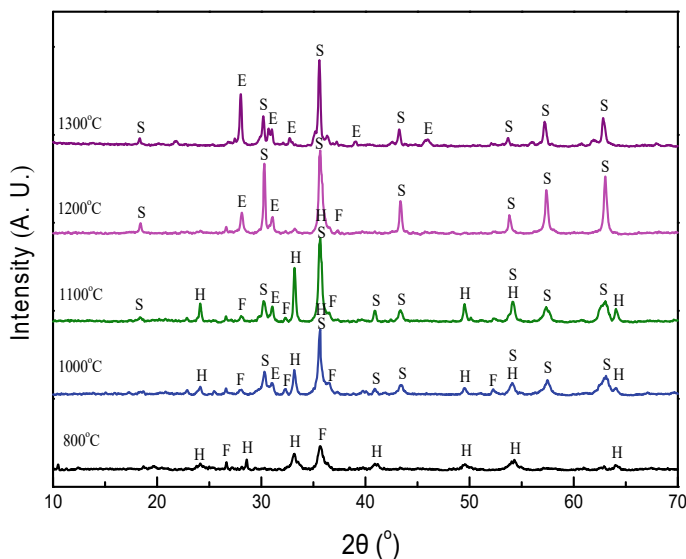


Fig. 4.3 XRD patterns of laterite ore with natural CaO content of 2 wt% roasted at different temperatures for 1 h in air. (*E* enstatite MgSiO_3 ; *F* forsterite Mg_2SiO_4 ; *H* hematite Fe_2O_3 ; *S* spinel MgFe_2O_4), reprinted from Ref. [9], copyright 2022, with permission from Elsevier Ltd

of Fe_2O_3 continuously decreased and then disappeared at 1200 °C. Meanwhile, the diffraction peaks of spinel and enstatite strengthened significantly. It indicated that the reaction rate of hematite and forsterite was accelerated by elevating temperature. When the temperature increased to 1300 °C, the diffraction peaks of forsterite disappeared. Except spinel, the main phase of roasting product existed in the form of enstatite.

Figure 4.4 shows the SEM–EDS analysis of the polished cross-section of laterite ore briquette with natural CaO content of 2 wt% roasted at 1300 °C for 1 h in air. It was shown that the particles of spinel and enstatite remained relatively independent (Fig. 4.4a). The bright white area denoted the magnesium–ferric spinel (Fig. 4.4b) and the dark gray area represented the enstatite. Some iron occurred in the serpentine still remained after roasting (Fig. 4.4c, d).

The laterite ore was mixed a certain proportion of calcium oxide and the content of calcium oxide in laterite mixture was defined as: (the mass of CaO addition + the mass of CaO in the raw laterite ore)/(the mass of raw laterite ore + the mass of CaO addition). The laterite ore briquettes with various CaO contents were then roasted at 1300 °C for 1 h in air. Figure 4.5 shows the XRD results of the roasted briquettes.

As shown in Fig. 4.5, the main phases of roasted sample changed accordingly as the CaO content increases. At the natural CaO content of 2 wt%, the main phases were enstatite (MgSiO_3) and spinel (MgFe_2O_4) after roasting. As the CaO content increased to 5 wt%, the diffraction peaks of enstatite and spinel increased and the diffraction peaks of diopside ($\text{CaMgSi}_2\text{O}_6$) were observed. When the CaO

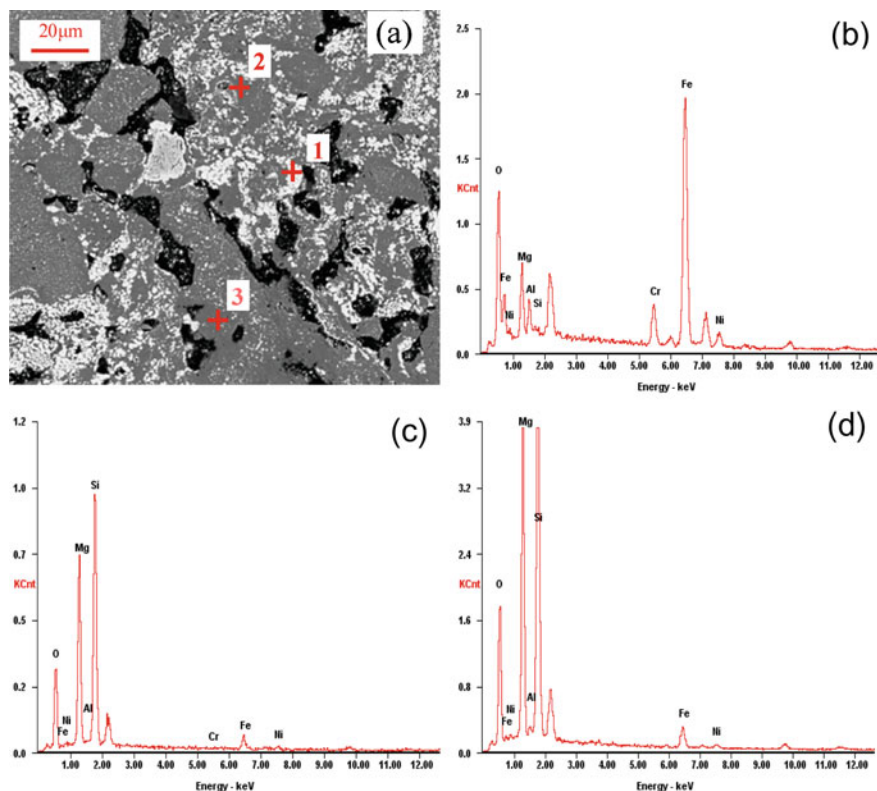


Fig. 4.4 SEM-EDS analysis of laterite ore briquette with natural CaO content of 2 wt% roasted at 1300 °C for 1 h in air. **a** backscattered electron image, **b** EDS spectrum of spot 1, **c** EDS spectrum of spot 2, and **d** EDS spectrum of spot 3, reprinted from Ref. [9], copyright 2022, with permission from Elsevier Ltd

content further increased to 10–15 wt%, the peak intensity of enstatite decreased while that of diopside was enhanced gradually. Meanwhile, the diffraction peaks of forsterite (Mg_2SiO_4) appeared. The results indicated that $\text{CaMgSi}_2\text{O}_6$ and Mg_2SiO_4 were generated by the reaction between the CaO and MgSiO_3 formed by lizardite decomposition.

With further increase in the CaO content, the diffraction peaks of diopside decreased and then disappeared as the CaO content exceeded 23 wt%. Meanwhile, the diffraction peaks of akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$) appeared. It indicated that after the reaction between CaO and MgSiO_3 , the excessive CaO would continue to react with $\text{CaMgSi}_2\text{O}_6$ to produce akermanite and merwinite. The diffraction peaks of spinel did not change significantly as the CaO content increased continuously, indicating that spinel remained stable during this process.

Figure 4.6 shows the micrographs of polished cross-section of roasted briquettes with various CaO contents. It can be concluded that the minerals in regions presented

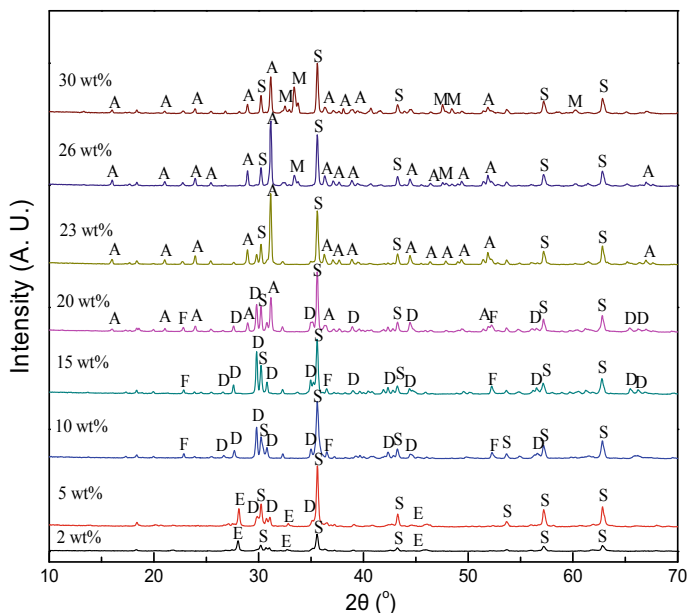


Fig. 4.5 XRD patterns of laterite ore with different CaO contents roasted at 1300 °C for 1 h in air. (A akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$; D diopside $\text{CaMgSi}_2\text{O}_6$; E enstatite MgSiO_3 ; F forsterite Mg_2SiO_4 ; M merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$; S spinel MgFe_2O_4), reprinted from Ref. [9], copyright 2022, with permission from Elsevier Ltd

in offwhite and dark gray were spinel and enstatite, respectively, when the CaO content was 2 wt%. When the CaO content was 10 wt%, enstatite disappeared and a large number of diopside (light gray area) appeared (Fig. 4.6b). The phases with high melting point such as spinel and forsterite were embedded in diopside (Fig. 4.7). Many large pores could be found in Fig. 4.6b which indicated that the melt phase was generated abundantly and bonded together with spinel and forsterite.

The laterite ore briquettes with different CaO contents were reduced at 1300 °C for 1 h in the 100% CO atmosphere. Figure 4.8 shows the XRD patterns of the reduced briquettes. The magnesium participated in the generation and transformation of all silicate minerals in the reductive roasting. With the addition of CaO, the silicates involving olivine $(\text{Mg, Fe})_2\text{SiO}_4$, diopside $\text{CaMgSi}_2\text{O}_6$, monticellite CaMgSiO_4 , akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ were present, depending on the amount of CaO. As shown in Fig. 4.8, olivine appeared firstly during the reduction process with the natural CaO content of 2 wt%. As the CaO content increased from 2 wt% to 10 wt%, olivine transformed gradually into monticellite and diopside. Besides, the diffraction peaks of diopside disappeared when the CaO content was 20 wt%. With further increase of CaO content, monticellite also disappeared while akermanite and merwinite were observed.

Figures 4.9 and 4.10 show the SEM–EDS analysis of polished cross-section of reduced briquettes with various CaO contents in the 100 vol% CO atmosphere. It can

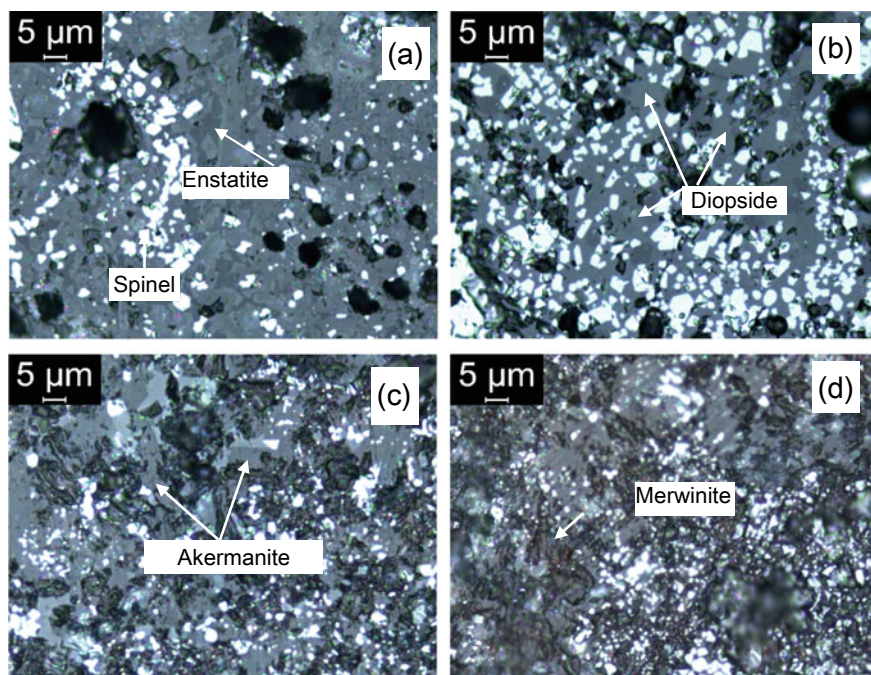


Fig. 4.6 Optical micrographs of laterite ore briquettes with different CaO contents roasted at 1300 °C for 1 h in air. **a** 2 wt% CaO, **b** 10 wt% CaO, **c** 20 wt% CaO, and **d** 30 wt% CaO, reprinted from Ref. [9], copyright 2022, with permission from Elsevier Ltd

be seen from Fig. 4.9a that the structure of main phases in the reduced sample with CaO content of 2 wt% was relatively complete, but melting occurred at the edge of the crystalline phase. According to the EDS analysis in Fig. 4.10a, the main phase was olivine. When the CaO content reached 10 wt% and 20 wt%, a large number of amorphous phases appeared in the reduction products and the crystals were further melted (Fig. 4.9b, c). According to the results of EDS in Fig. 4.10c, d, the main unmelted phase was monticellite and the akermanite was also included with the CaO content of 20 wt% (Fig. 4.10e). When the CaO content reached 26 wt%, wüstite appeared in the roasting product (Fig. 4.9d).

It should be noted that, due to roasting in a strong reductive atmosphere, the nickel oxide and iron oxide in the laterite ore could be reduced to metallic nickel and iron, respectively. Because nickel and iron are infinitely miscible, ferronickel appeared in the SEM images. By comparing Fig. 4.9a–d, after reductive roasting at 1300 °C, the particle size of ferronickel in the laterite ore increased firstly and then decreased with the increase of CaO content. When the CaO content was 10 wt%, the aggregation of ferronickel particle was obvious and the particle size of some ferronickel reached nearly 70 μm. It shows that the increase of calcium oxide was beneficial to the growth of ferronickel particles in the process of direct reduction. The detailed discussion is given in Sect. 4.4.

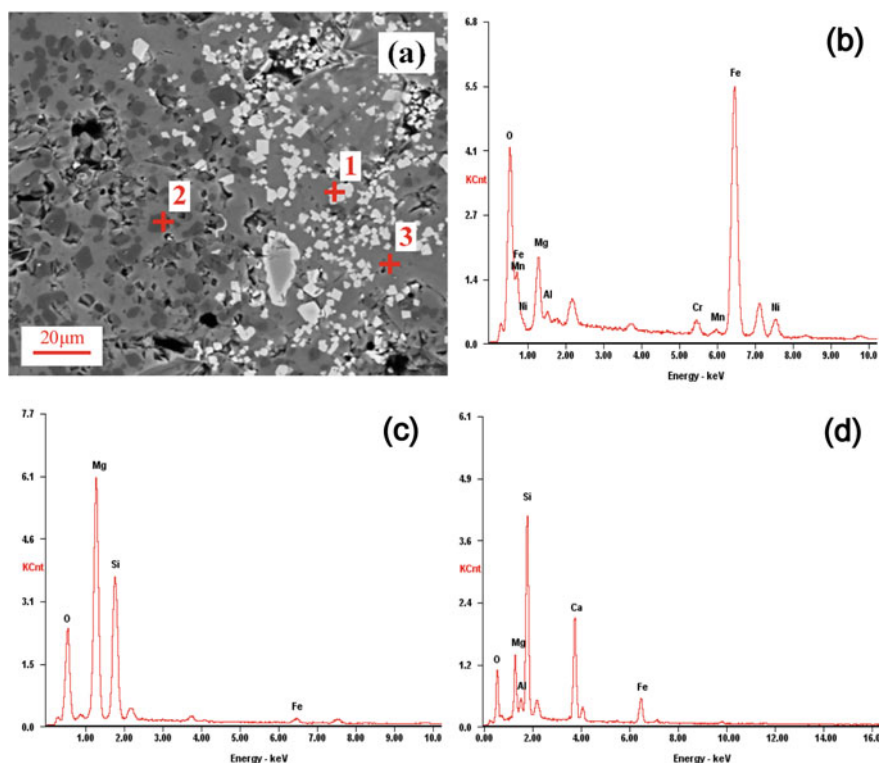


Fig. 4.7 SEM–EDS results of laterite ore briquettes with CaO content of 15 wt% roasted at 1300 °C for 1 h in air. **a** backscattered electron image, **b** EDS spectrum of spot 1, **c** EDS spectrum of spot 2, and **d** EDS spectrum of spot 3, reprinted from Ref. [9], copyright 2022, with permission from Elsevier Ltd

4.1.3 Effect of Roasting Temperature

The laterite ore briquettes were roasted at various temperatures for 1 h in the 100 vol% CO atmosphere and the phase compositions of the reduction products are shown in Figs. 4.11, 4.12 and 4.13, respectively. It was shown in Fig. 4.11 that the main phases included enstatite, olivine and ferronickel after the reductive roasting of laterite ore briquettes with CaO content of 2 wt% at 1100 °C. With the increase of roasting temperature to 1200 °C, the diffraction peaks of enstatite were weakened, while the diffraction peaks of olivine were strengthened. It indicated that increasing temperature was conducive to the combination of enstatite and forsterite to form olivine. As the temperature increased to 1300 °C, the enstatite and ferronickel disappeared and only the olivine phase appeared in the reduction products. At high temperature, the olivine crystals became more complete, which limited the reduction of iron oxides into metallic iron.

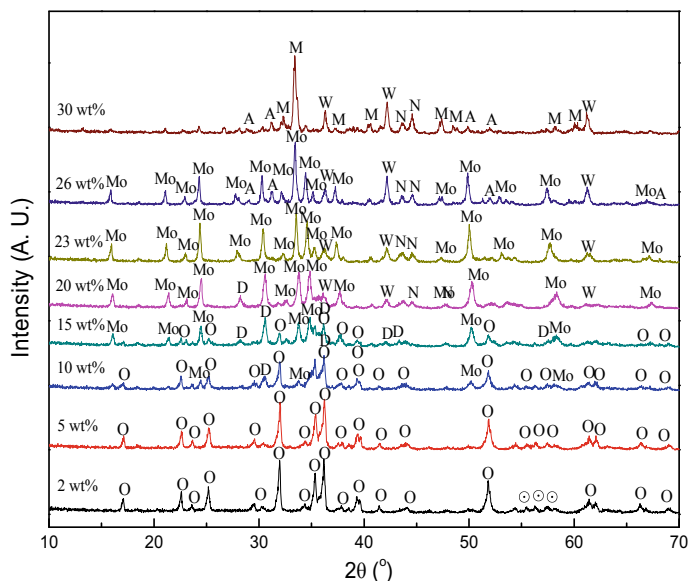


Fig. 4.8 XRD patterns of laterite ore briquettes with different CaO contents roasted at 1300 °C for 1 h in the 100 vol% CO atmosphere [13]. (A akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$; D diopside $\text{CaMgSi}_2\text{O}_6$; M merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$; N ferronickel Ni-Fe; Mo monticellite CaMgSiO_4 ; O olivine $(\text{Mg}, \text{Fe})_2\text{SiO}_4$; W wüstite $\text{Fe}_{0.92}\text{O}$), reprinted from Ref. [13], copyright 2022, with permission from The Iron and Steel Institute of Japan

When the CaO content increased to 15 wt%, there were enstatite, olivine, diopside and ferronickel in the reduction product at 1100 °C (Fig. 4.12). When the reduction temperature increased to 1200 °C, the diffraction peaks of enstatite disappeared. The diffraction peaks of ferronickel were also weakened, but the intensity of diffraction peaks of diopside increased. In addition, the diffraction peaks of monticellite were observed. The main phases of the products after roasting at 1300 °C was basically the same as those after roasting at 1200 °C and there was no significant difference in the diffraction peak intensity of each phase. It showed that the lower reduction temperature limited the reaction between calcium oxide with MgSiO_3 under the condition of increasing calcium oxide content. For example, although diopside was generated at the temperature of 1100 °C, its diffraction peak was weak. Increasing the temperature was conducive to the reactions involving calcium oxide. When the temperature exceeded 1200 °C, more calcium magnesium silicates existed in the roasting products.

When the CaO content was 26 wt%, the diffraction peaks of larnite (Ca_2SiO_4), olivine, akermanite and ferronickel appeared in the roasting product at 1100 °C (Fig. 4.13). When the temperature increased to 1200 °C, the diffraction peaks of larnite and olivine disappeared, along with the formation of monticellite. At 1300 °C, the diffraction peak intensity of monticellite increased, indicating its more

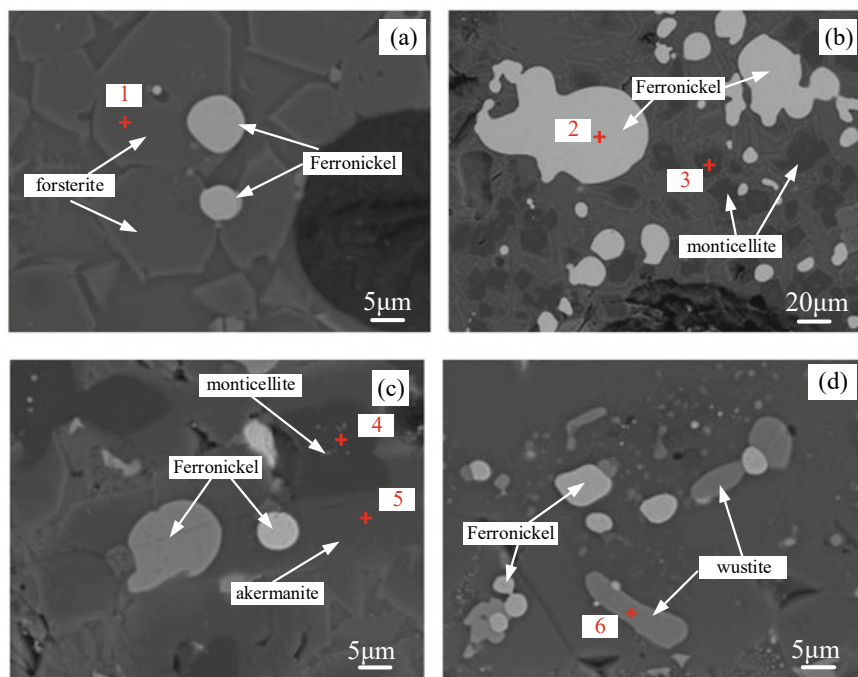


Fig. 4.9 SEM images of laterite ore briquettes with different CaO contents roasted at 1300 °C for 1 h in the 100 vol% CO atmosphere [13] (a 2 wt% CaO, b 10 wt% CaO, c 20 wt% CaO, and d 26 wt% CaO), reprinted from Ref. [13], copyright 2022, with permission from The Iron and Steel Institute of Japan

complete crystallization at higher roasting temperature. Meanwhile, the diffraction peaks of ferronickel in the reduction product were weakened and the diffraction peaks of wüstite appeared, which indicated that the reaction between iron-forsterite and magnesium-forsterite was strengthened at high temperature. As a result, the reduction of iron oxides was restricted.

By comparing the phase transformations of laterite ores at different reductive roasting temperatures (Figs. 4.11, 4.12 and 4.13), it was difficult for calcium oxide to react with the components of silicon, magnesium and iron in laterite ore at 1100 °C. Increasing the reduction temperature promoted the formation of calcium magnesium silicates. When the reduction temperature exceeded 1200 °C, the phases of laterite ore with the given CaO content were almost the same after reductive roasting, except for ferronickel. At the temperature of 1100 °C, the iron-bearing phases in laterite ore underwent dehydration and decomposition reactions to form hematite (Fig. 4.3), which could be further reduced in the reducing atmosphere. Therefore, the diffraction peaks of ferronickel in roasting products at 1100 °C were observed in Figs. 4.11, 4.12 and 4.13. With the increase of temperature, the olivine was generated by reactions of ferrous oxide (formed by reduction of hematite) and amorphous forsterite (formed by

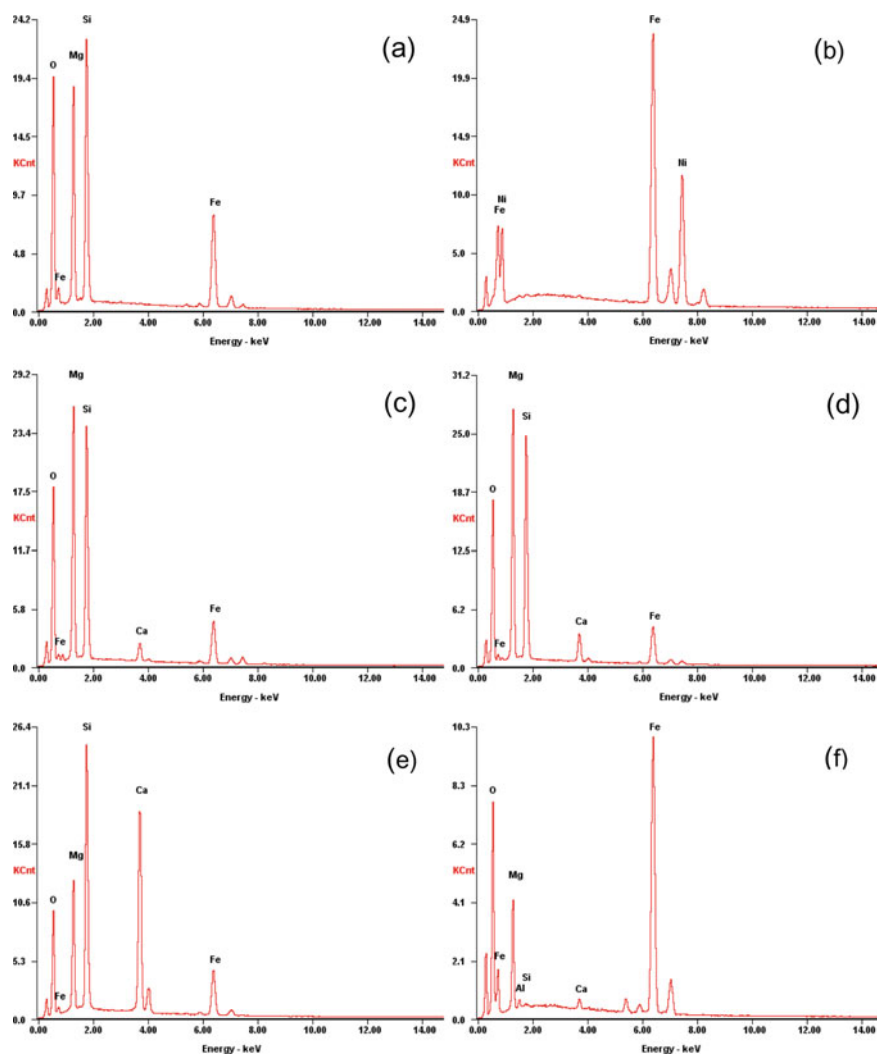


Fig. 4.10 EDS results of laterite ore briquettes with different CaO contents roasted at 1300 °C for 1 h in the 100 vol% CO atmosphere [13]. **a** EDS spectrum of spot 1, **b** EDS spectrum of spot 2, **c** EDS spectrum of spot 3, **d** EDS spectrum of spot 4, **e** EDS spectrum of spot 5, and **f** EDS spectrum of spot 6, reprinted from Ref. [13], copyright 2022, with permission from The Iron and Steel Institute of Japan

decomposition of serpentine), which limited the reduction of ferrous oxide, and the intensity of diffraction peaks of ferronickel decreased. However, with the increase of CaO content, the combination reaction of CaO with $\text{Mg}_2\text{SiO}_4/\text{MgSiO}_3$ produced calcium magnesium silicates, which restrained the formation of olivine.

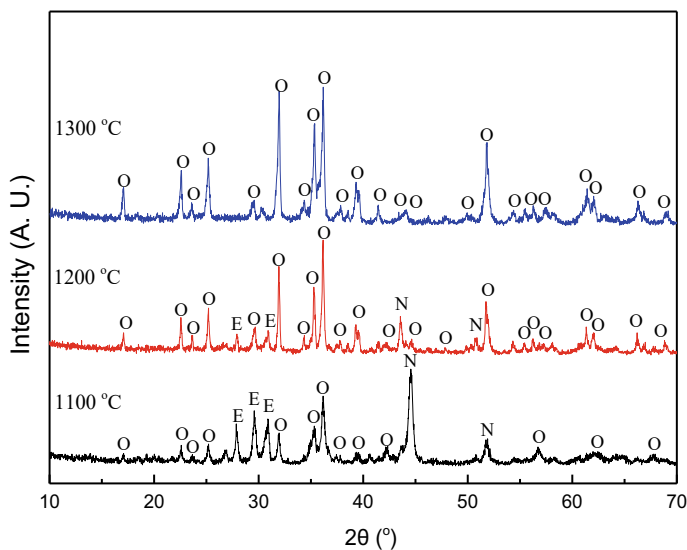


Fig. 4.11 XRD patterns of laterite ore briquettes with natural CaO content of 2 wt% roasted at different temperatures for 1 h in the 100 vol% CO atmosphere. (*E* enstatite MgSiO_3 ; *O* olivine $(\text{Mg}, \text{Fe})_2\text{SiO}_4$; *N* ferronickel Ni–Fe)

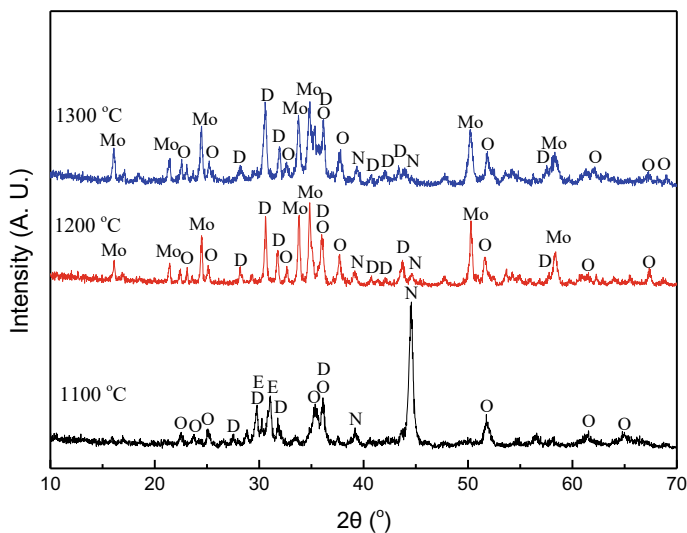


Fig. 4.12 XRD patterns of laterite ore briquettes with CaO content of 15 wt% roasted at different temperatures for 1 h in the 100 vol% CO atmosphere. (*D* diopside $\text{CaMgSi}_2\text{O}_6$; *E* enstatite MgSiO_3 ; *Mo* monticellite CaMgSiO_4 ; *N* ferronickel Ni–Fe; *O* olivine $(\text{Mg}, \text{Fe})_2\text{SiO}_4$)

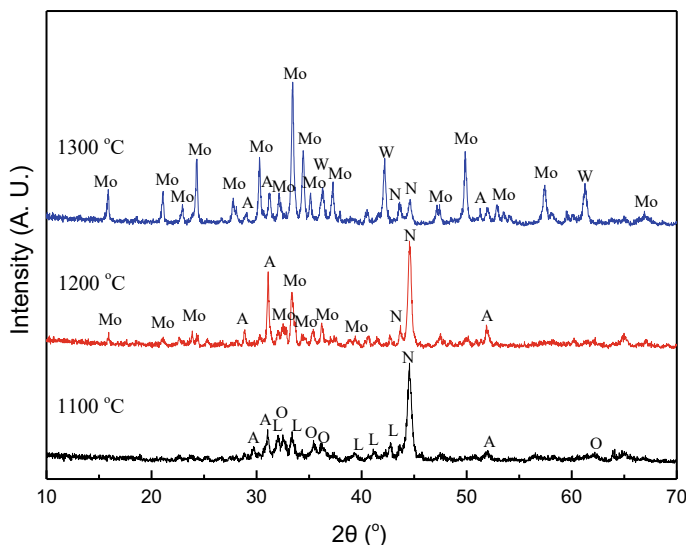


Fig. 4.13 XRD patterns of laterite ore briquettes with CaO content of 26 wt% roasted at different temperatures for 1 h in the 100 vol% CO atmosphere. (A akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$; L larnite Ca_2SiO_4 ; Mo monticellite CaMgSiO_4 ; N ferromagnetite Ni-Fe ; O olivine $(\text{Mg, Fe})_2\text{SiO}_4$; W wüstite $\text{Fe}_{0.92}\text{O}$)

4.1.4 Effect of CO Partial Pressure

The atmosphere affects the reduction of iron oxides in laterite ore during the roasting process. The laterite ores with fixed CaO content were roasted in the reducing atmosphere with different CO partial pressure. The XRD patterns of the roasting products are shown in Figs. 4.14, 4.15 and 4.16. It was found that the phases of laterite ore after reductive roasting have changed under different reducing atmospheres. In the weak reducing atmosphere, the phase changes were more obvious after roasting. However, the trend of phase transformation was consistent after increasing the CO partial fraction.

As the CaO content was 2 wt%, the phases included enstatite, olivine and spinel in the laterite ore roasted in the 25 vol% $\text{CO}/(\text{CO} + \text{CO}_2)$ atmosphere. However, only olivine existed at the CO partial fraction of above 75 vol%. It indicated that the hematite formed by decomposition of iron-bearing ore was easy to combine with MgSiO_3 and to form spinel in a relatively weak reductive atmosphere. The reduction of hematite to form divalent iron in a strong reducing atmosphere was conducive to the formation of olivine by the combination of ferrous iron and enstatite. As a result, the formation of spinel was restricted. Besides, the strong reducing atmosphere promoted the reduction of iron oxides. Therefore, only a small amount of olivine remained in the product after roasting in the 25 vol% $\text{CO}/(\text{CO} + \text{CO}_2)$ atmosphere, while the diffraction peaks of olivine was significantly enhanced as the diffraction peaks of

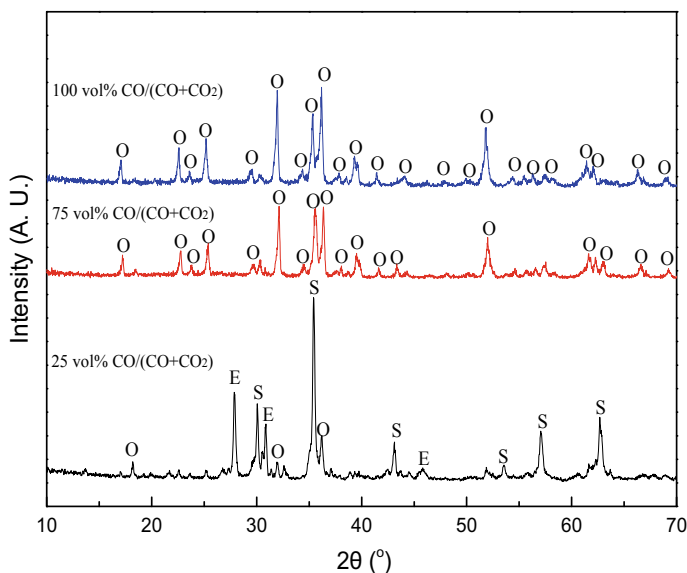


Fig. 4.14 XRD patterns of laterite ore briquettes with CaO content of 2 wt% roasted at 1300 °C for 1 h in different reducing atmospheres. (*E* enstatite MgSiO_3 ; *O* olivine $(\text{Mg, Fe})_2\text{SiO}_4$; *S* spinel MgFe_2O_4)

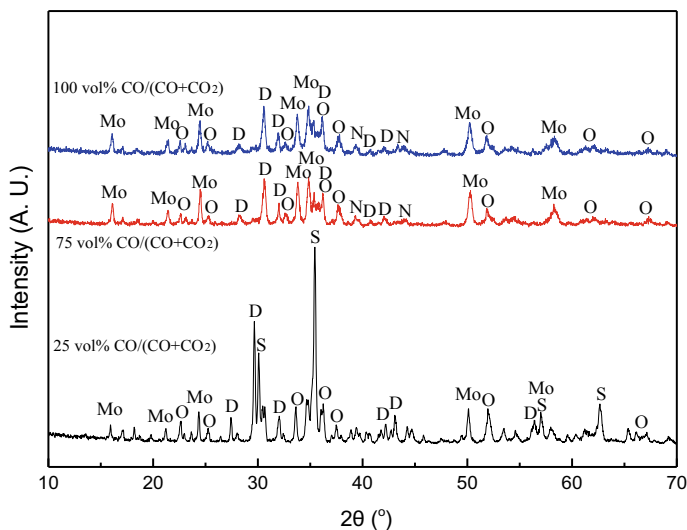


Fig. 4.15 XRD patterns of laterite ore briquettes with CaO content of 15 wt% roasted at 1300 °C for 1 h in different reducing atmospheres. (*D* diopside $\text{CaMgSi}_2\text{O}_6$; *Mo* monticellite CaMgSiO_4 ; *N* ferronickel Ni-Fe ; *O* olivine $(\text{Mg, Fe})_2\text{SiO}_4$; *S* spinel MgFe_2O_4)

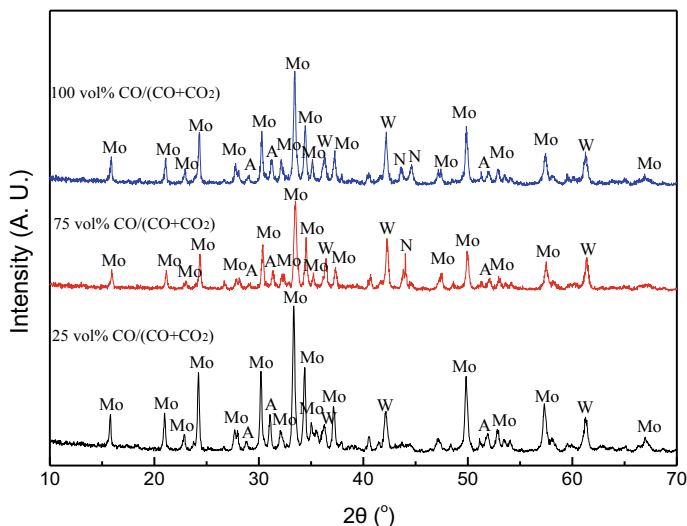


Fig. 4.16 XRD patterns of laterite ore briquettes with CaO content of 26 wt% roasted at 1300 °C for 1 h in different reducing atmospheres. (A akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$; Mo monticellite CaMgSiO_4 ; N ferronickel Ni-Fe; W wüstite $\text{Fe}_{0.92}\text{O}$)

enstatite disappeared, after roasting in the 75 vol% $\text{CO}/(\text{CO} + \text{CO}_2)$ and 100 vol.% CO atmosphere.

When the CaO content was 15 wt%, the main phases were transformed into olivine, diopside, monticellite and spinel in the product after roasting in the 25 vol% $\text{CO}/(\text{CO} + \text{CO}_2)$ atmosphere (Fig. 4.15). Compared with the reduced laterite ore briquettes with CaO content of 2 wt%, the diffraction peaks of enstatite disappeared, indicating that calcium oxide combined with enstatite to form diopside and monticellite. Under the strong reducing atmosphere, the diffraction peaks of diopside and monticellite existed, but the diffraction peaks of spinel disappeared. Besides, the diffraction peaks of ferronickel appeared. It was mainly because the binding capacity of calcium was stronger than that of iron divalent, which caused part of iron divalent to be dislocated and reduced to metallic iron. In addition, according to Figs. 4.14 and 4.15, the intensity of diffraction peaks of diopside in product after roasting in the 25 vol% $\text{CO}/(\text{CO} + \text{CO}_2)$ atmosphere was higher than that in the 75 vol% and 100 vol% $\text{CO}/(\text{CO} + \text{CO}_2)$ atmospheres, indicating that low CO partial fraction in the reducing atmosphere was conducive to the formation of diopside.

When the CaO content reached 26 wt%, the main phases of the products obtained in different reduction atmospheres had no significant change. They mainly included monticellite, akermanite and wüstite (Fig. 4.16). A part of wüstite was further reduced to metallic iron in the reducing atmosphere. The diffraction peaks of ferronickel existed after reduction in the 75 vol% and 100 vol% $\text{CO}/(\text{CO} + \text{CO}_2)$ atmospheres.

4.2 Characteristic Fusion Temperatures of Laterite Ore

The phase composition of laterite ore is usually changed under different roasting conditions. The newly formed phases have different melting properties, leading to significant changes in the melting characteristics of laterite ore. The characteristic fusion temperatures and their influencing factors of laterite ore were studied.

The dried laterite ore was mixed with a certain quantity of CaO and then the mixture was shaped by a mold into pyramids (1.5 g, bottom side length of 5 mm and vertical height of 12 mm). The photo of the furnace for the tests is shown in Fig. 4.17a. CO gas was replenished to the horizontal tube (diameter of 40 mm and length of 550 mm) in the furnace and the inlet gas flow was fixed at 350 L/h. The pyramid was placed on a corundum plate and heated in a given reducing atmosphere from 900 °C to 1500 °C. The temperature rising curve is shown in Fig. 4.18. The shape change of the tested sample was continuously recorded by a camera every 10 s during the experiment.

The characteristic fusion temperatures included (1) deformation temperature (T_D), determined by the temperature at which the tip of the pyramid became spherical or curved; (2) sphere temperature (T_S), determined by the temperature at which the whole pyramid deformed to be hemispheric; (3) flow temperature (T_F): determined by the temperature at which the pyramid melted until the vertical height was lower than 1.5 mm (Fig. 4.17b).

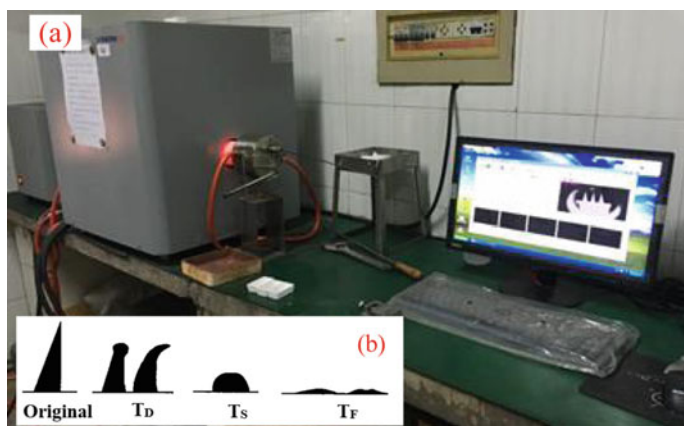


Fig. 4.17 (a) Apparatus for determination of fusion characteristic temperatures and (b) change of sample shape with increasing temperature

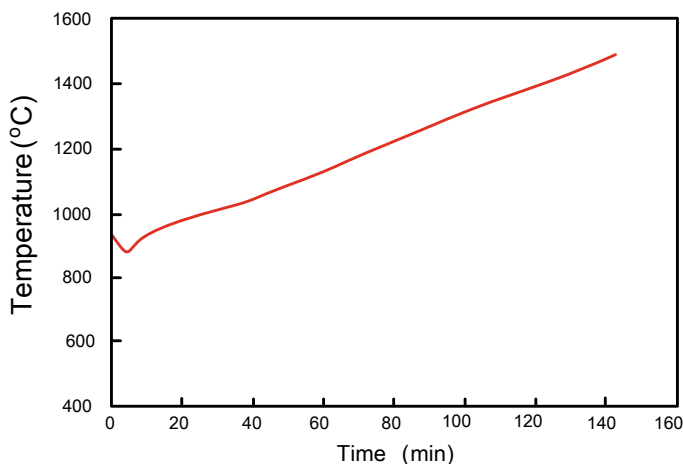


Fig. 4.18 Temperature rising curve of laterite ore during determination of fusion characteristic temperatures

4.2.1 Effect of CaO Content

The characteristic fusion temperatures of laterite ore with different CaO contents in air are shown in Fig. 4.19. It indicated that CaO had significant effects on the characteristic fusion temperatures. The characteristic fusion temperatures of the laterite ore with CaO content of 2 wt% (natural CaO content), namely T_D , T_S , and T_F , were 1385 °C, 1395 °C and 1407 °C, respectively. As the CaO content increased from 2 wt% to 30 wt%, the characteristic fusion temperatures (T_D , T_S , and T_F) of the laterite ore decreased initially and then increased with a valley at the CaO content of 15 wt%, at which T_D , T_S , and T_F were 1272 °C, 1299 °C and 1306 °C, respectively. It indicated that the temperature of liquid phase formation of laterite ore could be decreased by over 100 °C under the suitable CaO addition.

The variation tendency of characteristic fusion temperatures was consistent with the phase transformation of the roasted laterite ores with various CaO contents (Fig. 4.4). The main phases of roasted laterite ore with CaO content of 2 wt% were the high-melting point enstatite and spinel, which resulted in the high characteristic fusion temperatures. However, the formation of diopside was achieved with the optimal CaO content of 15 wt%, while an excessive CaO was detrimental to the stability of diopside, leading to the formation of akermanite and merwinite. Thus, the characteristic fusion temperatures would increase with the transformation of diopside into akermanite and merwinite.

The characteristic fusion temperatures of laterite ores with different CaO contents in the 100 vol% CO atmosphere are shown in Fig. 4.20. It indicates that the characteristic fusion temperatures (T_D , T_S , and T_F) of the laterite ore decreased initially and then increased, as the CaO content increased from 2 wt% to 30 wt%. Apparently, the changing trend of characteristic fusion temperatures in the 100 vol% CO

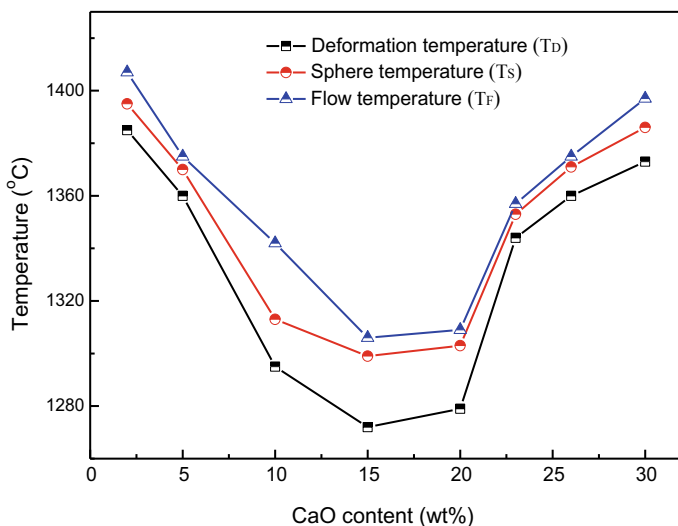


Fig. 4.19 Characteristic fusion temperatures of laterite ore with different CaO contents in air, reprinted from Ref. [9], copyright 2022, with permission from Elsevier Ltd

atmosphere was similar to that in air although the characteristic fusion temperatures of laterite ore in the 100 vol% CO atmosphere were lower. As shown in Fig. 4.20, the laterite ore with CaO content of 2 wt% was featured by high characteristic fusion temperatures in the 100 vol% CO atmosphere, with the T_D , T_S , and T_F of 1229 °C, 1373 °C and 1391 °C, respectively. Compared with the counterparts obtained in air, the T_S was decreased by 160 °C in a 100 vol% CO atmosphere, while the T_D and T_F were decreased by 20 °C. Due to the formation of ferrous oxide during roasting, the liquid phase amount in the laterite ore in reducing atmosphere was higher than that in air at the given temperature, resulting in an obvious change of the deformation temperature.

By increasing the CaO content, the characteristic fusion temperatures tended to decrease. The phase transformation in Fig. 4.10 confirmed that diopside was formed in the CaO content range of 10–15 wt%, leading to lower characteristic fusion temperatures. With the CaO content of 10 wt%, T_D , T_S , and T_F reached their minimum values (1157 °C, 1243 °C and 1267 °C, respectively). Compared with laterite ore with CaO content of 2 wt%, T_D , T_S , and T_F were decreased by 72 °C, 130 °C and 124 °C, respectively.

When the CaO content exceeded 15 wt%, the characteristic fusion temperatures of laterite showed an increasing trend with the increase of CaO content (Fig. 4.20). With the CaO content of 23 wt%, T_D was 1278 °C, which was higher than that of laterite ore with natural CaO content. With the CaO content of 30 wt%, T_S and T_F were 1377 °C and 1389 °C, respectively, which were close to those of laterite

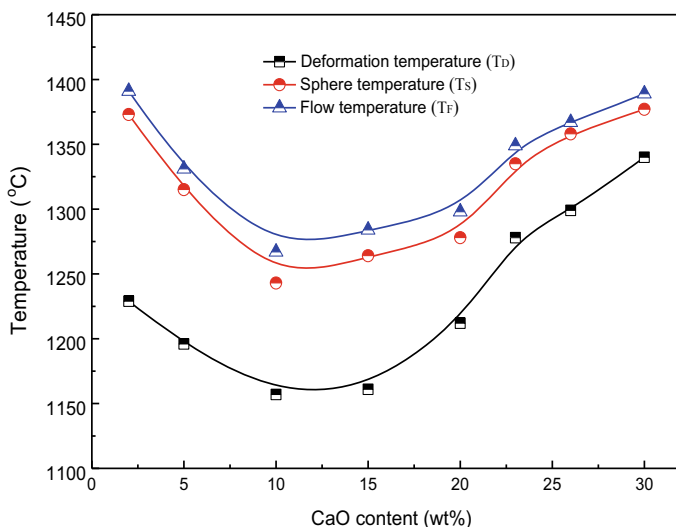


Fig. 4.20 Characteristic fusion temperatures of laterite ore with different CaO contents in the 100 vol% CO atmosphere [13], reprinted from Ref. [13], copyright 2022, with permission from The Iron and Steel Institute of Japan

with natural CaO content. Evidently, the transformation from diopside and monticellite into akermanite and merwinite contributed to increase of characteristic fusion temperatures.

Obviously, regulating the phase formation during reductive roasting of laterite ore by adding an appropriate amount of CaO could lower characteristic fusion temperatures, which promoted the formation of liquid phase in the high-temperature processing of laterite ore.

4.2.2 Effect of CO Partial Pressure in Reducing Atmosphere

Figure 4.21 shows the characteristic fusion temperatures of laterites ore detected in different reducing atmosphere. The characteristic fusion temperatures of laterite ores with various CaO contents showed the consistent trend in different reducing atmospheres. T_D , T_S , and T_F increased with the increase of CO partial fraction in the atmosphere. According to Fig. 4.22, the Fe(II) content in reduced laterite ore decreased under the stronger reducing atmosphere. Hence, the characteristic fusion temperatures increased with increasing CO partial fraction. The high CO partial pressure promoted the reduction of iron oxides to metallic iron, resulting in the reduction of ferrous content in roasted laterite ore. However, the ferrous content was improved after roasting in the weak reducing atmosphere, which was beneficial to reduction of the characteristic fusion temperature of laterite ore.

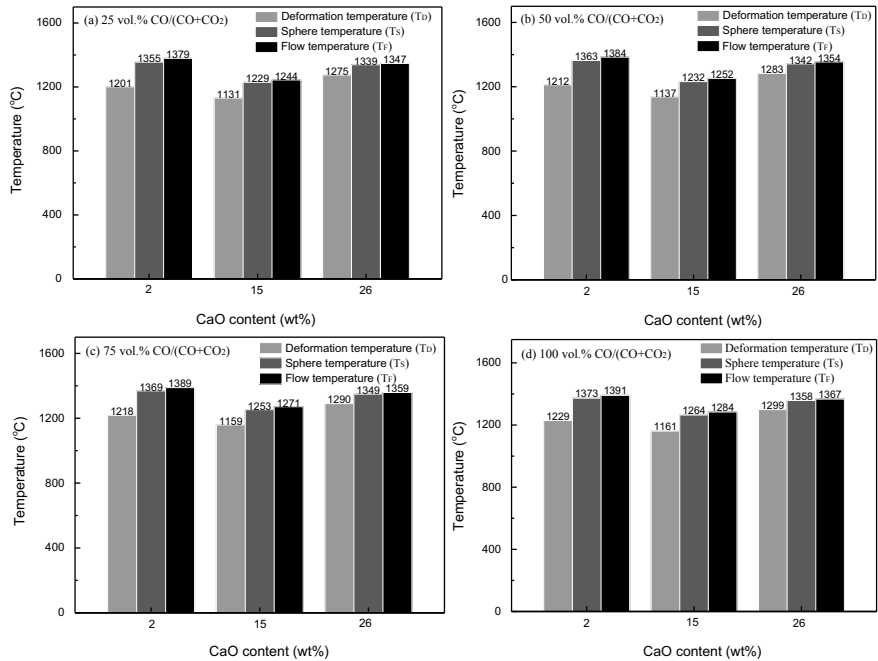


Fig. 4.21 Characteristic fusion temperatures of laterite ore in different reducing atmospheres

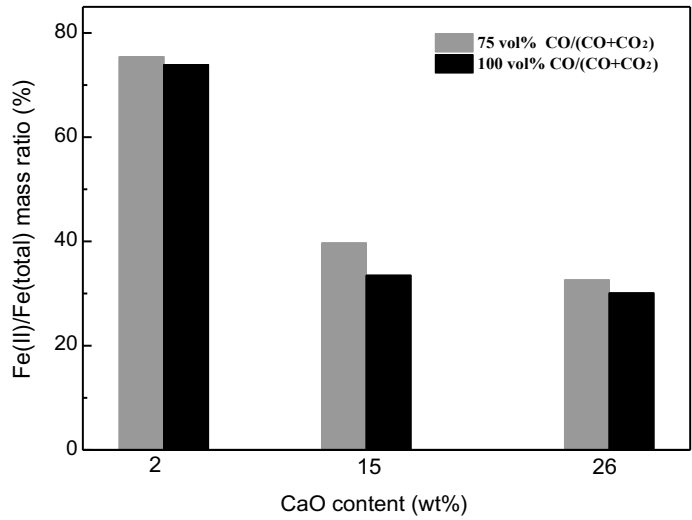


Fig. 4.22 Mass ratios of Fe(II) to Fe(total) in the laterite ore with different CaO contents after reduction at 1200 °C for 1 h, reprinted from Ref. [25], copyright 2022, with permission from Springer Nature

When the CaO content was 2 wt%, the characteristic fusion temperatures including T_D , T_S , and T_F , decreased from 1229 °C, 1373 °C and 1391 °C to 1201 °C, 1355 °C and 1379 °C, respectively, with the CO partial fraction in reducing atmosphere changing from 100 vol% to 25 vol%. These characteristic fusion temperatures decreased by about 20 °C. When the CaO content was 15 wt%, T_D , T_S , and T_F , decreased from 1161 °C, 1264 °C and 1284 °C in the 100 vol% CO atmosphere to 1131 °C, 1229 °C and 1244 °C in the 25 vol% CO/(CO + CO₂) atmosphere, respectively, with decreases of more than 30 °C.

4.2.3 Effect of FeO Content

Ferrous oxide was obtained firstly by decomposition of ferric oxalate and a certain proportion of ferrous oxide was then mixed into the laterite ore. The characteristic fusion temperatures of the mixture were measured in the 100 vol% N₂ atmosphere and the results are shown in Fig. 4.23. It is shown that the characteristic fusion temperatures gradually decreased with the increase in the ferrous oxide content. At the FeO content of 0, T_D , T_S , and T_F were 1390 °C, 1404 °C and 1550 °C, respectively, while these values decreased to 1345 °C, 1376 °C and 1486 °C, respectively, when the FeO content of 30 wt%. The enstatite and spinel with high melting point were the main phases of laterite ore after roasting, causing high characteristic fusion temperatures. Increasing ferrous content promoted the generation of olivine with lower melting point. As a result, characteristic fusion temperatures decreased.

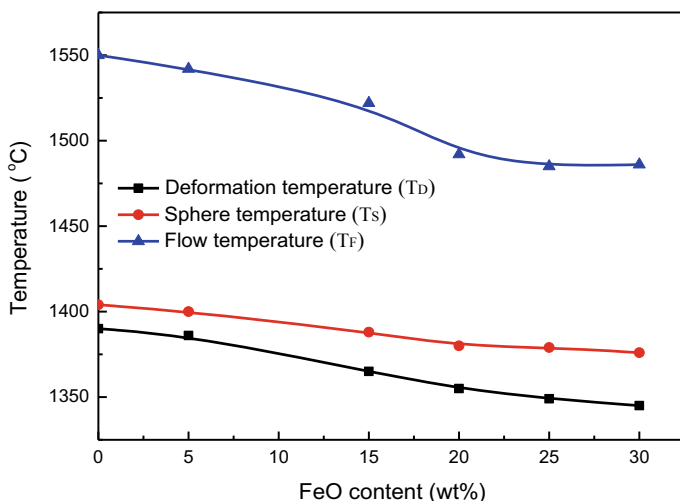


Fig. 4.23 Characteristic fusion temperatures of laterite ores with different FeO contents in the 100 vol% N₂ atmosphere

4.3 Regulation Technology of Softening–Melting Performance of Laterite Ore

The current pyrometallurgical processes of ferronickel from laterite ore include the blast furnace smelting process, rotary kiln–electric furnace smelting process and Krupp–Renn process (namely rotary kiln direct reduction process). In the Krupp–Renn process, the aggregation and growth of ferronickel particles are crucial, and a certain amount of liquid phase in the feed is required to ensure sufficient aggregation of the ferronickel particles during the reductive roasting and then efficient separation ferronickel from slag. Besides, in the blast furnace smelting process, a certain amount of liquid phase is also necessary during sintering, which is used as binder phase to improve mineralization of sinter, improving output and quality of sinter. However, the high silica and magnesia contents in laterite ore often restrain the formation of the melting phase, due to generation of refractory silicate minerals with high melting points during roasting. As a result, the migration of ferronickel particles is limited and the growth of ferronickel particles is hard during reductive roasting in the Krupp–Renn process. In the sintering process, the mineralization of sinter is difficult and the yield of sinter is low.

Based on the above studies, it indicates that the contents of calcium, magnesium, aluminum and silicon in laterite (especially the CaO content) play an important role in the phase transformation and melting characteristics of laterite during high-temperature roasting. Particularly, during the reductive roasting, the ferrous oxide formed by reduction of hematite combine with silica to form the olivine phase. At a low CaO content, the combination of enstatite/olivine forms monticellite. With the increase of CaO content, CaO react with enstatite/olivine to form diopside with low melting point, lowering the characteristic fusion temperature of laterite ore.

In conclusion, in order to solve the problems of liquid phase formation in the Krupp–Renn process and sintering process, a new technology based on regulation of quaternary basicity of laterite was developed. The generated diopside replaced forsterite during roasting, decreasing the temperature of the liquid phase formation. As expected, the growth of ferronickel particles was strengthened and the separation of ferronickel from slag was improved in the Krupp–Renn process. The mineralization of sinter was also strengthened and the quality of sinter was improved.

4.4 Regulation Technology Applied in the Krupp–Renn Process

4.4.1 Growth Behaviors of Ferronickel Particles

4.4.1.1 Microstructure

The laterite ore briquettes with various quaternary basicities were reduced at 1100–1300 °C for 1 h in the 100 vol% CO atmosphere. The optical microstructures of these reduced briquettes are shown in Figs. 4.24, 4.25 and 4.26. When the laterite briquettes were reduced at 1100 °C, the structure of minerals remained relatively integrated. The liquid phase was not available at 1100 °C. Hence, the growth of ferronickel particles was restricted, as revealed by abundant tiny Ni–Fe particles in Fig. 4.24. Obviously, the growth of ferronickel particles was inefficient by the solid phase diffusion during reductive roasting. It was difficult to separate ferronickel from slag by common physical separation methods.

From Fig. 4.25, the quantities of ferronickel particles in the reduced briquettes with natural quaternary basicity of 0.5 and quaternary basicity of 0.8 were greatly

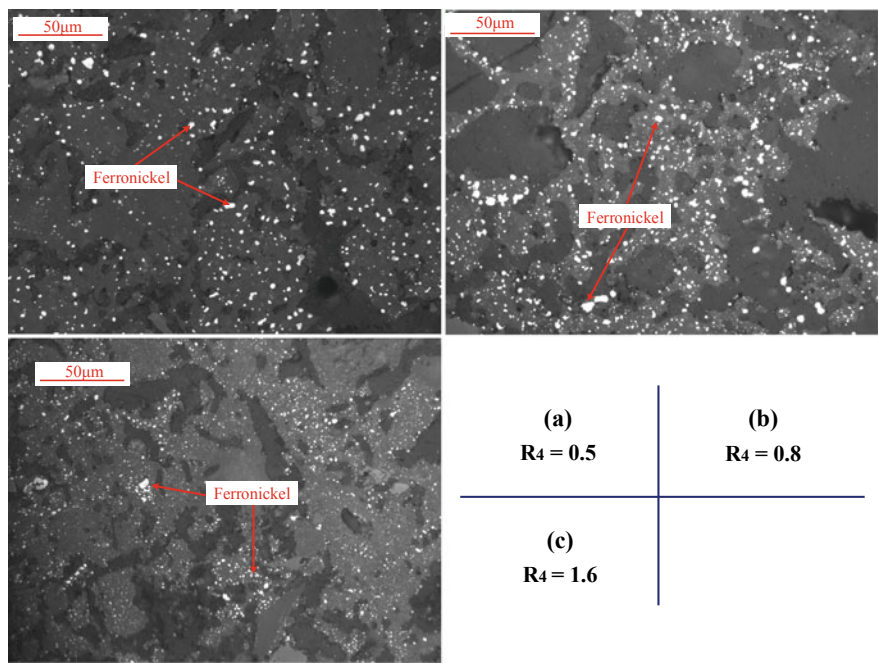


Fig. 4.24 Optical microstructures of the laterite ore briquettes with various quaternary basicities after reduction at 1100 °C for 1 h in the 100 vol% CO atmosphere, reprinted from Ref. [25], copyright 2022, with permission from Springer Nature

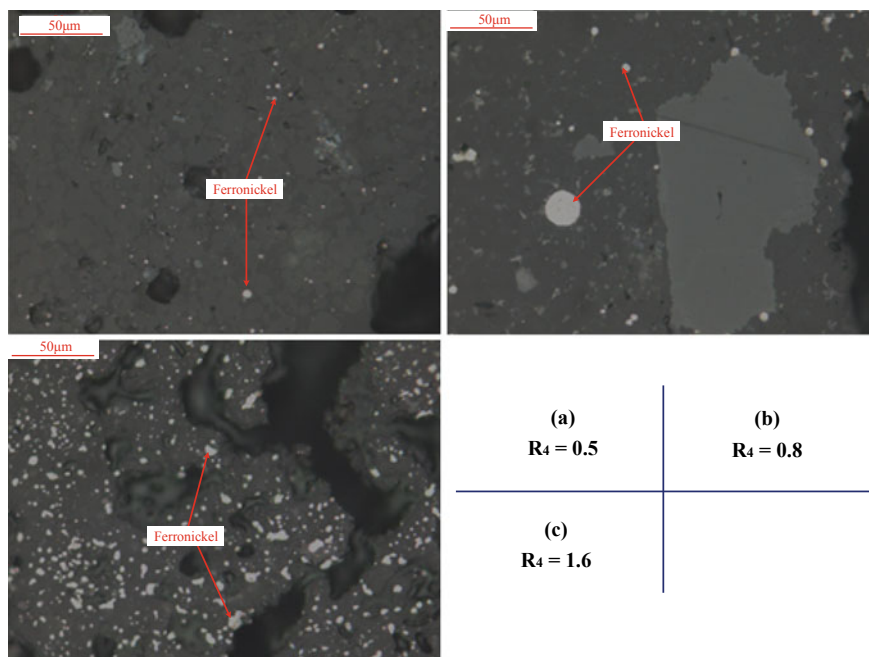


Fig. 4.25 Optical microstructures of the laterite ore briquettes with various quaternary basicities after reduction at 1200 °C for 1 h in the 100 vol% CO atmosphere, reprinted from Ref. [25], copyright 2022, with permission from Springer Nature

decreased. Conversely, many fine ferronickel particles still remained in the briquette with the quaternary basicity of 1.6 (Fig. 4.25c). The generation of liquid phase at 1200 °C resulted in densification of the briquette with the quaternary basicity of 0.8 and the ferronickel particles size increased evidently. A part of ferronickel particles grew to about 20 μm (Fig. 4.25b).

Increasing temperature to 1300 °C caused serious densification of all the reduced laterite ore briquettes, due to large amounts of liquid phase formation (Fig. 4.26). The size of ferronickel particles further increased, especially in the briquette with the quaternary basicity of 0.8, and a part of ferronickel particles reached about 50 μm (Fig. 4.26b). Besides, some wüstite appeared in the reduced briquette with the quaternary basicity of 1.6 (Fig. 4.26c), as confirmed by the XRD patterns in Fig. 4.13.

Liquid phase promoted ferronickel particles growth. The SEM images of the reduced briquettes with various quaternary basicities at 1100–1200 °C for 1 h in the 100 vol.% CO atmosphere are shown in Fig. 4.27. It can be seen from Fig. 4.27a, b that the structure of raw materials had no obvious change after reductive roasting at 1100 °C. Tiny ferronickel particles which distributed randomly were observed. The sizes of ferronickel particles were below 5 μm and 10 μm with the quaternary basicities of 0.5 and 0.8, respectively. When the reduction temperature reached 1200 °C,

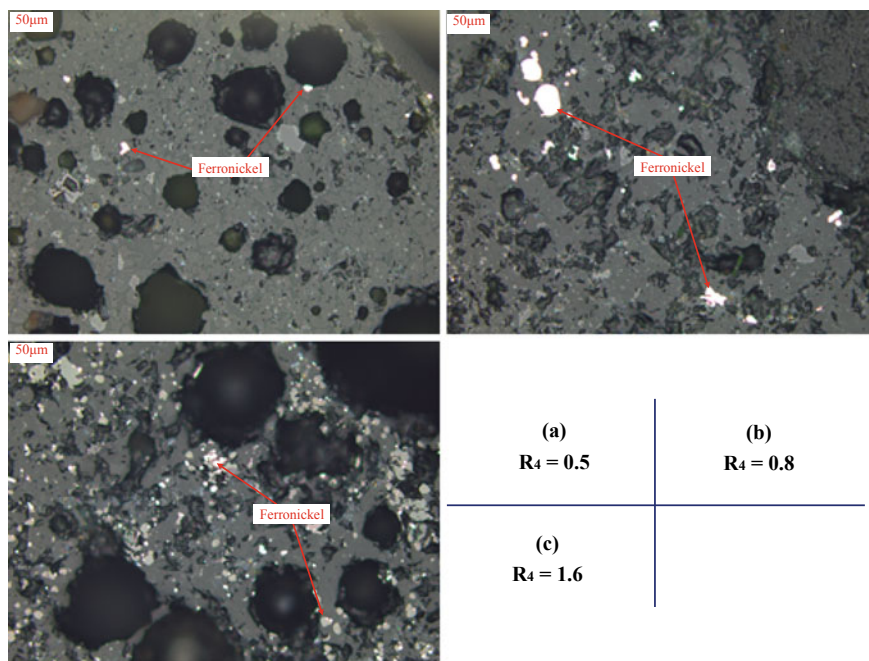


Fig. 4.26 Optical microstructures of the laterite ore briquettes with various quaternary basicities after reduction at 1300 °C for 1 h in the 100 vol% CO atmosphere, reprinted from Ref. [25], copyright 2022, with permission from Springer Nature

the structure of the material was destroyed and the ferronickel particles aggregated and grew up (as shown in Fig. 4.27c, d). Some particles exceeded 15 μm in the reduced briquette with the quaternary basicity of 0.8.

4.4.1.2 Volume Ratio of Ferronickel Particles

The size of ferronickel particles was calculated by using an optical microscope (LEICA MDI5000 M, Germany) and the software Image-Pro Plus 6.0. Firstly, 16 zones were divided evenly in both edge part and middle part (1/2 radius) of the cross-section of reduced briquettes (as shown in Fig. 4.28) and then 2 photos (200 $\times$ 150 μm) in each zone (32 photos in total for each specimen) were taken and saved in a computer. The quantity and area of ferronickel particles in the photos were then detected by using the software Image-Pro Plus 6.0. By assuming the particles were spherical in the three-dimensional space, they could be regarded as round in the two-dimensional space [26, 27]. The equivalent diameter and volume of each particle could be calculated. Provided that the area of the edge zone (S_2) was 2 times larger than that of the middle zone (S_1), the area of photo taking zone was extremely small compared to that of briquette cross-section, likewise the volume ratio. Therefore,

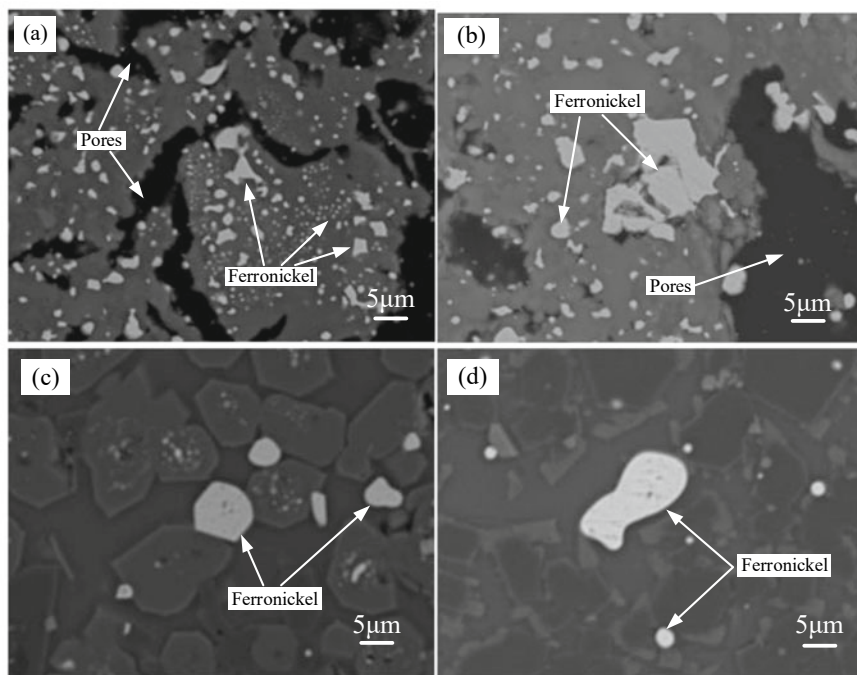


Fig. 4.27 SEM images of the laterite ore briquettes after reduction for 1 h in the 100 vol% CO atmosphere. **a** 1100 °C, $R_4 = 0.5$, **b** 1100 °C, $R_4 = 0.8$, **c** 1200 °C, $R_4 = 0.5$, and **d** 1200 °C, $R_4 = 0.8$ [13], reprinted from Ref. [13], copyright 2022, with permission from The Iron and Steel Institute of Japan

the total volume of ferronickel particles could also be calculated using the following equation:

$$V_{total-FeNi} = V_{1-FeNi} + 2V_{2-FeNi} \quad (4.1)$$

where $V_{total-FeNi}$ is the total volume of ferronickel particles in the reduced briquette; V_{1-FeNi} is the volume of ferronickel particles in the middle zone, and V_{2-FeNi} is the volume of ferronickel particles in the edge zone.

The sizes of ferronickel particles in the reduced briquettes at various reductive temperatures were determined and the results are shown in Figs. 4.29, 4.30 and 4.31. The regulation of quaternary basicity of laterite ore improved the ferronickel particles size. As shown in Fig. 4.29, the particle size of ferronickel was below 9 μm in the reduced briquette with quaternary basicity of 0.5 at 1100 °C. The growth of ferronickel particles was impeded due to lack of liquid phase during reductive roasting at 1100 °C. When the quaternary basicity was 1.0, the maximum particle size reached about 30 μm and the particles with this size accounted for more than 3% of the total ferronickel particles. Further increase of quaternary basicity to 1.6

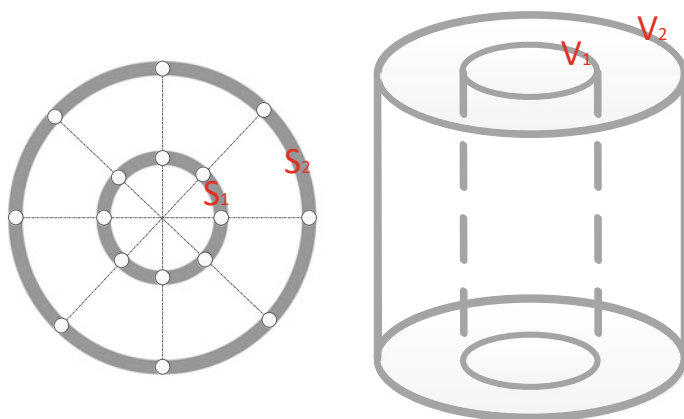


Fig. 4.28 Schematic diagram showing the photo taking zones (circles in white) in the cross-section of reduced briquettes [13], reprinted from Ref. [13], copyright 2022, with permission from The Iron and Steel Institute of Japan

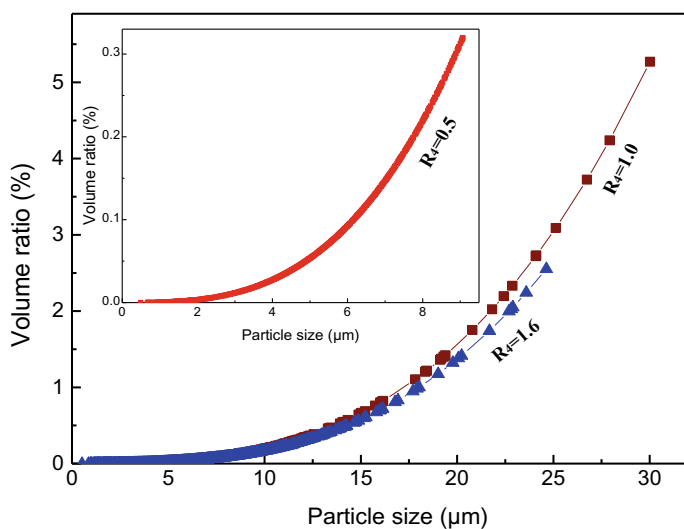


Fig. 4.29 Volume ratios of various ferronickel particle sizes in the laterite ore briquettes after reduction at 1100 °C for 1 h in the 100 vol% CO atmosphere, reprinted from Ref. [25], copyright 2022, with permission from Springer Nature

caused the decrease of the maximum particle size to about 25 μm. Meanwhile, the volume ratio decreased to about 2.5%.

When the temperature was elevated to 1200 °C, the overall size of ferronickel particles in the reduced briquettes increased slightly (as shown in Fig. 4.30), indicating the aggregation of fine ferronickel particles with generation of liquid phase

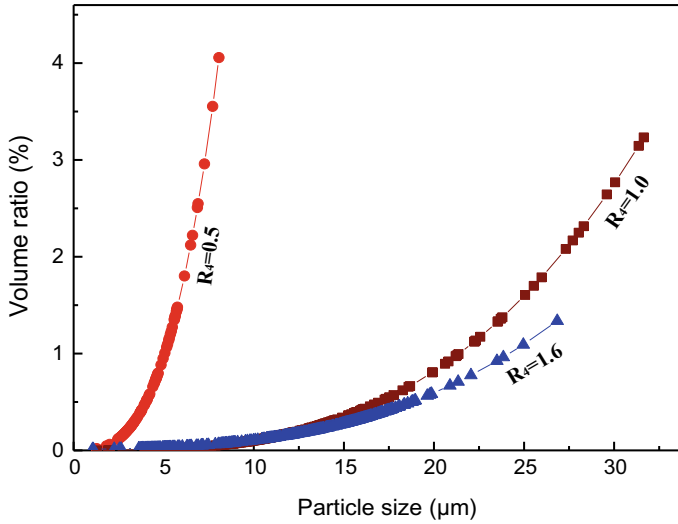


Fig. 4.30 Volume ratios of various ferronickel particle sizes in the laterite ore briquettes after reduction at 1200 °C for 1 h in the 100 vol% CO atmosphere, reprinted from Ref. [25], copyright 2022, with permission from Springer Nature

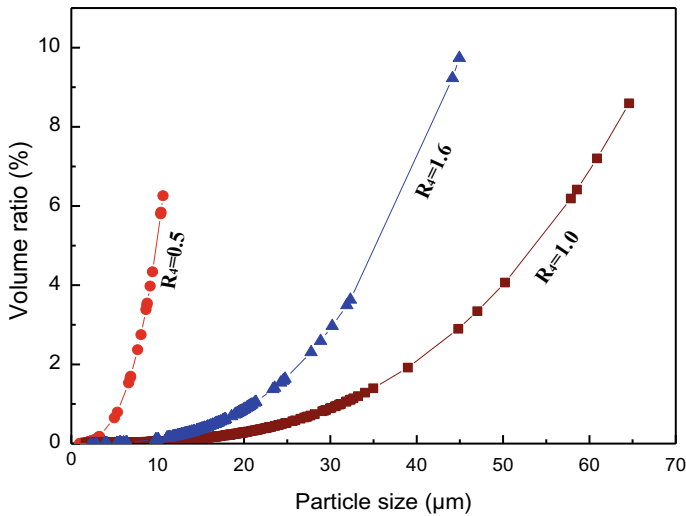


Fig. 4.31 Volume ratio of various ferronickel particle sizes in the laterite ore briquettes after reduction at 1300 °C for 1 h in the 100 vol% CO atmosphere, reprinted from Ref. [25], copyright 2022, with permission from Springer Nature

at this temperature. Specially, at the quaternary basicity of 0.5, the volume ratio of ferronickel particle sizes with 6–9 μm increased to about 4%. The maximum particle size reached about 32 μm and 27 μm , respectively, while the corresponding volume ratio decreased to 3.5% and 1.4%, respectively, at quaternary basicities of 1.0 and 1.6.

As shown in Fig. 4.31, the size of ferronickel particles in the reduced briquettes increased evidently at the temperature of 1300 °C. The maximum size of ferronickel particle was about 10 μm in the reduced briquette with quaternary basicity of 0.5 and its volume ratio reached about 7%. When the quaternary basicity was 1.0, the maximum size of ferronickel particle increased to about 65 μm and the volume ratio increased to 9%. Besides, at a quaternary basicity to 1.6, the maximum particle size was about 45 μm and the volume ratio increased to 10%.

4.4.1.3 Average Size of Ferronickel Particles

Based on the relationship between cumulative volume ratios and diameter of ferronickel particle, the diameter corresponding to the cumulative volume ratio of 50% was defined as the apparent mean particle size (L) of ferronickel. The true average particle size (D) was then corrected by Eq. (4.2) [28].

$$D = \frac{4}{\pi} L \quad (4.2)$$

Figure 4.32 shows the average size of ferronickel particles in the reduced briquettes with various quaternary basicities at 1300 °C for 1 h in the 100 vol% CO atmosphere. The average size of ferronickel particles firstly increased and then decreased in the quaternary basicity range from 0.5 to 1.6 and the average particle size reached the maximum value of about 31–34 μm in the quaternary basicity range 0.8–1.2. These results confirmed that lowering fusion temperature promoted the growth of ferronickel particles. It further indicated that the product quality of the Krupp–Renn process could be improved by adjusting and optimizing the quaternary basicity of laterite ores.

The results of the effect of temperature on the average size of ferronickel particles in the briquettes after reductive roasting are shown in Fig. 4.33. It was shown that the average size was gradually increased with reduction temperature. However, the amounts of liquid phase were not the same at different reduction temperatures. Hence, the growth mechanism of ferronickel particles was also different during reductive roasting. At 1100 °C, due to the absence of liquid phase, the aggregation of ferronickel particles was only realized by solid phase diffusion. The growth of ferronickel particle was limited.

With the increase of reduction temperature, the amount of liquid phase gradually increased. The fine ferronickel particles aggregated through the liquid channel. As the mass transfer condition was improved, the average size of ferronickel particles increased.

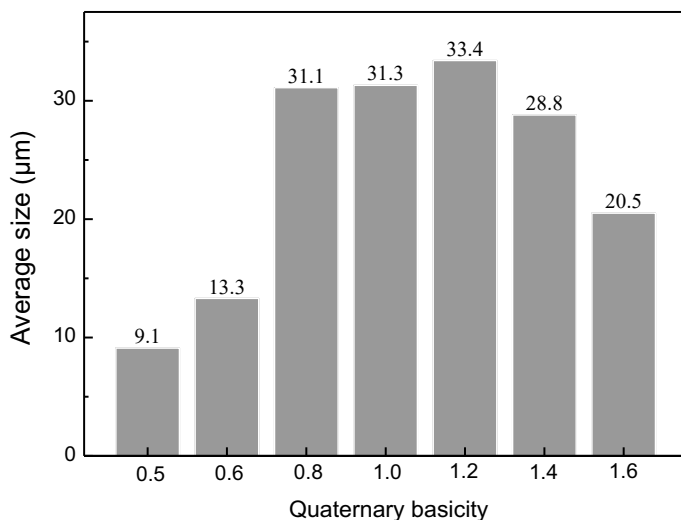


Fig. 4.32 Average sizes of ferronickel particles in the laterite ore briquettes with various quaternary basicities after reduction at 1300 °C for 1 h in the 100 vol% CO atmosphere [13], reprinted from Ref. [13], copyright 2022, with permission from The Iron and Steel Institute of Japan

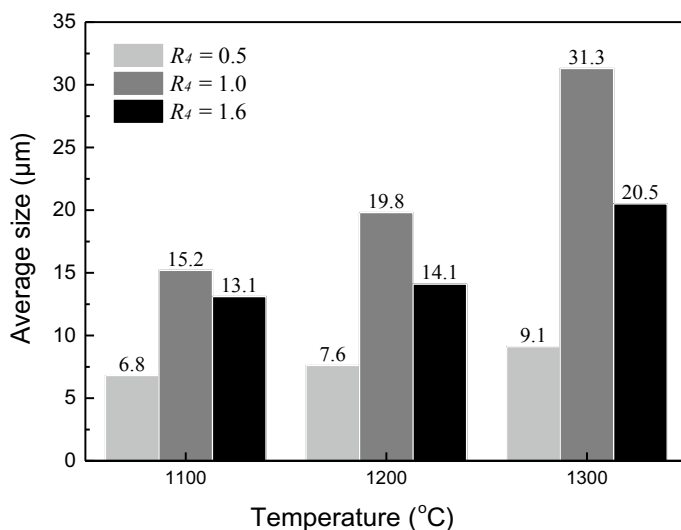


Fig. 4.33 Average sizes of ferronickel particles in the laterite ore briquettes after reduction at different temperatures for 1 h in the 100 vol% CO atmosphere, reprinted from Ref. [25], copyright 2022, with permission from Springer Nature

The average size of ferronickel particles in the reduced briquettes with quaternary basicities of 0.5 maintained below 9 μm in the temperature range 1100–1300 $^{\circ}\text{C}$ because of the low liquid phase formation at these temperatures (Fig. 4.33). When the quaternary basicity was 1.0, the average size of the particles significantly increased from 15.2 μm to 31.4 μm as the reduction temperature increased from 1100 $^{\circ}\text{C}$ to 1300 $^{\circ}\text{C}$. However, as the quaternary basicity reached 1.6, the average size increased from 13.1 μm to 20.5 μm .

Except for the quaternary basicity of laterite ore, the atmosphere also affected the characteristic fusion temperature of the ore, which had an impact on the growth of ferronickel particles during reductive roasting. The average sizes of ferronickel particles of briquettes reduced under different atmospheres are shown in Fig. 4.34. Although the characteristic fusion temperature of laterite ore detected in the 100 vol% CO atmosphere was higher than that in the 75 vol% CO/(CO + CO₂) atmosphere, the average size of ferronickel particles after reduction in the 100 vol% CO atmosphere was higher than that in the 75 vol% CO/(CO + CO₂) atmosphere at given reduction temperature and time. The main reason was that the reduction of iron oxides was strengthened in the 100 vol% CO atmosphere. Meanwhile, the ferrous oxide content decreased and the amount of metallic iron increased (Fig. 4.22). The particle size of ferronickel particles increased due to the aggregation of more metallic iron particles.

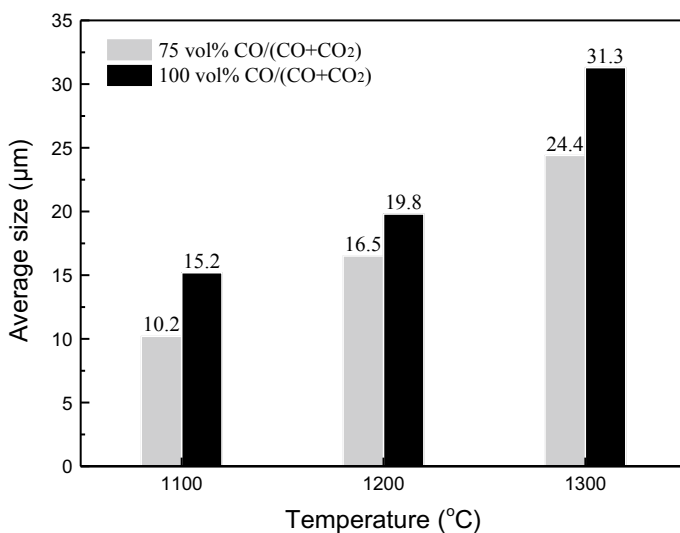


Fig. 4.34 Average sizes of ferronickel particles in the reduced briquette with quaternary basicity of 1.0 at 1300 $^{\circ}\text{C}$ for 1 h in different atmospheres

4.4.2 Grinding–Magnetic Separation of Ferronickel from Reduced Laterite Ore

The regulation of the quaternary basicity had a significant effect on the growth of ferronickel particles during reductive roasting. With the suitable quaternary basicity, the size of ferronickel particles increased significantly after reductive roasting, which was conducive to the subsequent separation of ferronickel from slag.

4.4.2.1 Effect of Quaternary Basicity

The laterite ores with different quaternary basicities were reduced firstly at 1200 °C for 1 h using lignite as reducing agent and then the ferronickel was separated from the reduced products after grinding followed by magnetic separation with magnetic intensity of 1000 Gs. The effect of quaternary basicity on the recovery of ferronickel is shown in Fig. 4.35. With the natural quaternary basicity of 0.5, the recovery of ferronickel was unsatisfied. The nickel and iron grades in the magnetic concentrate were 3.5 wt% and 64.8 wt%, respectively, with the recovery percentages of 47.3% and 75.4%, respectively. By increasing the quaternary basicity of laterite ore, these indexes were improved obviously. When the quaternary basicity was in the range 0.8–1.2, the nickel and iron grades in the concentrate increased to about 7 wt% and above 80 wt%, respectively, and the recovery percentages of nickel and iron were higher than 81%. For example, at quaternary basicity of 1.0, the nickel and iron grades in the concentrate reached 7.1 wt% and 83.7 wt%, respectively, with the recovery percentages of 83.3% and 85.8%, respectively.

4.4.2.2 Effect of Reduction Temperature

The ferronickel recoveries from laterite ores with quaternary basicities of 0.5 and 1.0 reduced in the temperature range 1100–1300 °C are shown in Figs. 4.36 and 4.37, respectively. The grades and recoveries of nickel and iron in the magnetic concentrate increased with reduction temperature. At the natural quaternary basicity of 0.5, as the reduction temperature increased from 1100 °C to 1300 °C, the nickel and iron grades in the concentrate increased from 2.9 wt% to 3.9 wt% and from 61.3 wt% to 71.4 wt%, respectively, and the recovery ratios of nickel and iron increased from 36.9% to 61.6% and from 67.1% to 87.9%, respectively. It indicated that the low liquid phase production limited the growth of ferronickel particles at quaternary basicity of 0.5, resulting in poor ferronickel recovery.

With the quaternary basicity of 1.0, the recovery of ferronickel from reduced laterite ore improved with increasing reduction temperature (Fig. 4.37). When the temperature increased from 1100 °C to 1200 °C, the nickel and iron grades in the concentrate increased from 6.9 wt% to 7.1 wt% and from 70.1 wt% to 83.7 wt%, respectively. Their recovery percentages increased from 75.3% to 83.3% and from

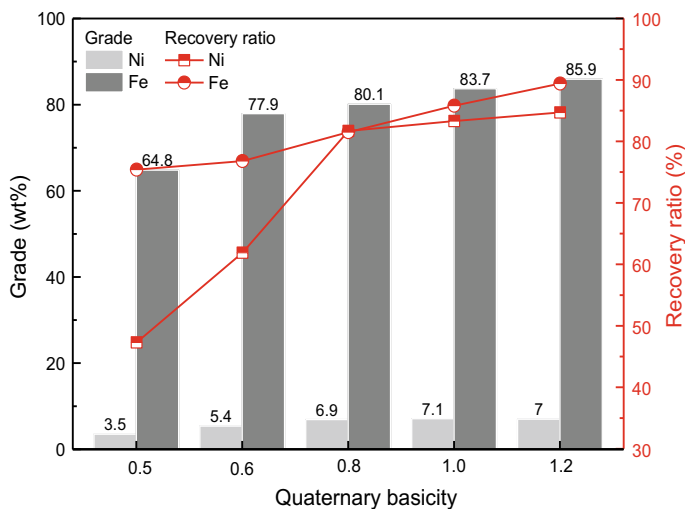


Fig. 4.35 Effect of quaternary basicity on the recovery of ferronickel from laterite ore reduced at 1200 °C for 1 h

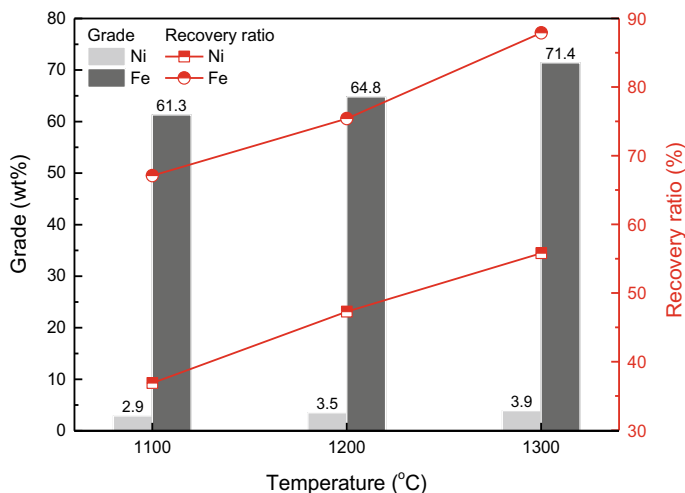


Fig. 4.36 Effect of reduction temperature on the recovery of ferronickel from laterite ore with quaternary basicity of 0.5 reduced for 1 h

66.4% to 85.8%, respectively. The increase of quaternary basicity enhanced the liquid phase formation and promoted the reduction of iron oxides. Therefore, the grades and recoveries of nickel and iron in the concentrate were improved, especially the grade and recovery of iron. When the reduction temperature increased to 1300 °C, the grades of nickel and iron in the concentrate also increased, but the recovery

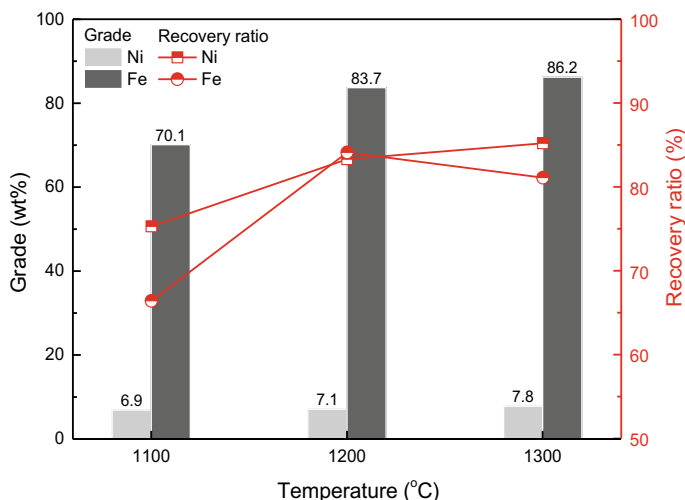


Fig. 4.37 Effect of reduction temperature on the recovery of ferronickel from laterite ore with quaternary basicity of 1.0 reduced for 1 h

percentage of iron decreased. The main reason was that the excessive liquid phase led to the formation of laterite ore lump. The reduction atmosphere was weakened in the internal of lump, which limited the reduction of iron oxides. As a result, the recovery of iron after magnetic separation was decreased.

4.4.3 Comparison with the “Oheyama Process”

During the reductive roasting, the quaternary basicity of laterite ore and reductive temperature affects the growth of ferronickel particles. By regulating the quaternary basicity of laterite ore and controlling the reduction temperature, the amount of liquid phase produced can be changed during roasting, affecting the growth of ferronickel particles. It should be noted that the above studies on the growth of ferronickel particles were carried out in the laboratory-scale furnace. However, the feeds are in a state of motion during the actual ferronickel production process in the rotary kiln, which is conducive to the reduction of nickel and iron oxides and to the growth of ferronickel particles.

Figure 4.38 shows the relationship between the particle size of ferronickel particles and reduction temperature obtained by simulation of the process in Nippon Yakin Kogyo Co., Ltd., Oheyama [3]. The raw laterite ore had the total nickel and iron contents of 2.07 wt% and 14.67 wt%, respectively, and the natural quaternary basicity was 0.5. The other conditions were as follows: addition of anthracite (65 kg/t of ore) and limestone (50 kg/t of ore, CaO content of 55.08 wt%) [3], quaternary basicity of mixtures of 0.55, and reduction time of 2 h. As shown in Fig. 4.38, the

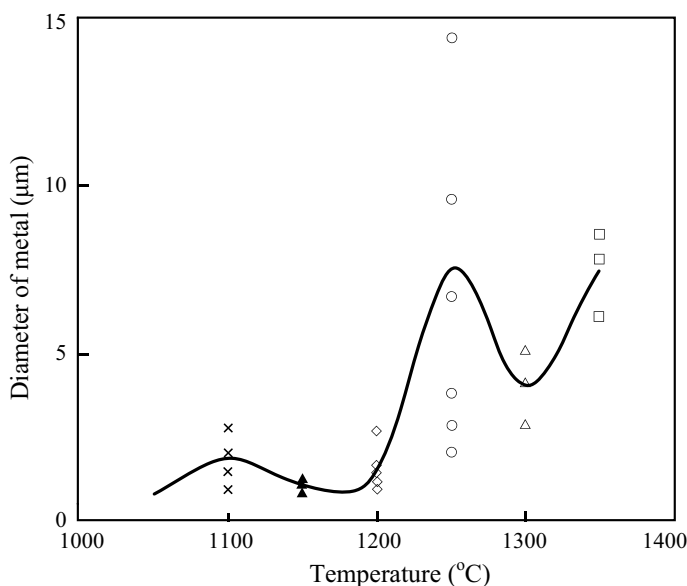


Fig. 4.38 Relationship between the diameter of metal obtained by SEM observation and temperature [3]

diameter of ferronickel particles showed an increasing trend with reductive roasting temperature although the particles were smaller than 10 μm . Under the experimental conditions, the main phases of reduced laterite ore were olivine and enstatite. Only little liquid phase appeared at temperatures below 1350 $^{\circ}\text{C}$ and the aggregation of ferronickel particles was limited. This is the main reason why the maximum roasting temperature in rotary kiln should be increased to 1400–1450 $^{\circ}\text{C}$ to increase the size of ferronickel particles in the “Oheyama process”.

According to the results in Table 4.2, by controlling the quaternary basicity of 0.8–1.2 to promote the formation of diopside with low melting point, the growth of ferronickel particles could be improved at a low reduction temperature. Specifically, the average size of ferronickel particles of reduced laterite ores with quaternary basicities of 0.8–1.0 at 1100 $^{\circ}\text{C}$ exceeded that of ferronickel particles after reductive roasting at 1250–1350 $^{\circ}\text{C}$, as shown in Fig. 4.38. At a higher reduction temperature, the average size of ferronickel particles with diopside as the main low melting point phase was obviously larger than that having olivine as the main low melting point phase.

The current practices showed that by considering only the liquid phase formation during reductive roasting, it is possible to produce excessive liquid phase that leads to the ring formation in rotary kiln [17, 18]. In view of this fact, although the average size of ferronickel particles increased significantly with the quaternary basicity of 0.8–1.2 at 1300 $^{\circ}\text{C}$, the remarkable fusion occurred in the briquettes at this temperature because of formation of a large amount of liquid (Fig. 4.39). Hence, it was not suitable

Table 4.2 Average sizes of ferronickel particles in the reduced briquettes under different reduction conditions

Quaternary basicity	Temperature (°C)	Time (min)	Atmosphere	Average size (μm)
0.8	1100	60	100 vol% CO	14.5
	1200			15.9
	1300			31.0
1.0	1100	60	100 vol% CO	15.2
	1200			19.8
	1300			31.3
1.2	1100	60	100 vol% CO	18.0
	1200			27.2
	1300			33.4

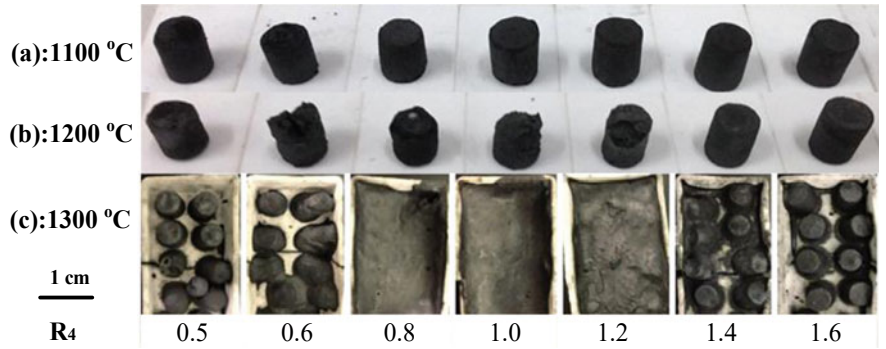


Fig. 4.39 Appearance of reduced briquettes with various basicities in the 100 vol% CO atmosphere [13]

for the practical production. Therefore, it is necessary to match the relationship between the quaternary basicity of laterite ore and the reduction temperature. On the premise of ensuring the ferronickel particles growth, the production of liquid phase should be controlled in an appropriate range to ensure the growth of ferronickel particles and to avoid ring formation in the kiln.

In conclusion, an enhanced ferronickel particle growth technology was adopted to regulate the quaternary basicity of laterite ore in the range 0.8–1.2 to ensure the formation of diopside in the process of reductive roasting, which can significantly reduce the roasting temperature to 1200–1250 °C required by the Krupp–Renn process. Compared with the temperature of 1400–1450 °C in the “Oheyama process”, the lower reduction temperature can reduce the requirement for rotary kiln, enabling simpler operations. Meanwhile, laterite ore can generate an appropriate amount of liquid phase during roasting, which can ensure the aggregation of ferronickel particle under the above conditions. On the other hand, the laterite ore lump can still maintain

the original morphology. There is no obvious melting which reduces ring formation in rotary kiln.

4.5 Regulation of Sintering Process

The sintering process is that the solid particles in the sinter mixture have solid reactions at high temperature caused by the combustion of coke/anthracite. Firstly, a part of solid particles generate the low-melting point compounds and then these compounds form molten matter through the liquid phase reaction. The consolidation of the rest of solid particles is realized through the liquid phase condensation. The sintering mineralization process consists of solid phase reactions, liquid phase formation and condensation crystallization. The liquid phase consolidation is the main method of sintering. Hence, the composition and physicochemical properties of liquid phase during the sintering process largely determine the output and quality of sinter [29]. The conditions for the formation of liquid phase include the phase and chemical compositions of the raw materials, atmosphere and temperature of the material bed. The purpose of sintering operation is to produce an appropriate amount of liquid phase by adjusting the sintering mixture and operation conditions [30] to obtain the sinter with suitable strength and metallurgical properties.

Unlike traditional iron ore, laterite ore has high contents of silicon and magnesium and low contents of iron and nickel. It is difficult to generate sufficient liquid phase with a natural basicity. The liquid phase can only be formed by further increasing the sintering temperature or by adding flux. In the sintering process, increasing the sintering temperature will increase the production cost and put forward higher requirements on the equipment. Therefore, the reasonable method is to add flux to reduce the melting temperature of feed, which promotes the formation of liquid phase at a lower sintering temperature.

During the sintering of iron ore, the calcium and silicon components affect the phase transformation and liquid phase formation in the sintering process. Hence, the binary basicity (CaO/SiO_2 mass ratio) of the mixture is usually regulated. However, the components of magnesium, silicon, aluminum and calcium have significant effects on the phase transformation and liquid phase formation during sintering of laterite ore. The quaternary basicity ($(\text{CaO} + \text{MgO})/(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ mass ratio) should be controlled in the sintering of laterite ore. Due to the high contents of magnesium and silicon, the aluminum content should be maintained in the appropriate range. In this case, the quaternary basicity of the sintering mixture can be regulated via adjusting the content of calcium oxide. The formation of diopside with low melting point can be obtained through the optimization of ore proportioning. The formation of liquid phase will be promoted during sintering. As a result, the sintering process of laterite ore can be strengthened with better quality of sinter.

4.5.1 Sintering of Saprolitic Laterite Ore

4.5.1.1 Raw Materials

The raw materials for sintering pot tests included saprolitic laterite ore, quick lime, coke breeze and return fine. The chemical composition of saprolitic laterite ore is listed in Table 4.1. Quick lime was used as flux. As shown in Table 4.3, its CaO content was 75.3 wt%. The particle size was about 85 wt% of the particles passing a 3 mm-pore size sieve and nearly 75 wt% of the particles had the size of 1–3 mm, as shown in Table 4.4.

Coke breeze was used as fuel in the sintering tests. Table 4.5 shows its chemical composition. According to the proximate analysis, the fixed carbon content of coke breeze was 82 wt%. Nearly 80% of particles size was below 1 mm (Table 4.6).

The return fine was used to ensure consistent material composition in the tests. The sinter produced from saprolitic laterite ore was crushed to ensure that the particle size did not exceed 5 mm. The chemical composition and size distribution of return fine are shown in Tables 4.7 and 4.8, respectively.

Table 4.3 Chemical composition of quick lime (wt%)

Composition	Fe _{total}	CaO	MgO	Al ₂ O ₃	SiO ₂	Loss on ignition
Content	0.08	75.33	4.13	0.05	2.87	17.03

Table 4.4 Particle size distribution of quick lime (wt%)

Size	5–3 mm	3–1 mm	1–0.25 mm	<0.25 mm
Proportion	0.08	75.33	4.13	0.05

Table 4.5 Chemical composition of coke breeze (wt%)

Composition	Fe _{total}	CaO	MgO	Al ₂ O ₃	SiO ₂	Loss on ignition
Content	2.52	0.35	0.08	4.55	6.02	86.87

Table 4.6 Particle size distribution of coke breeze (wt%)

Size	5–3 mm	3–1 mm	1–0.25 mm	<0.25 mm
Proportion	7.14	12.49	38.31	38.56

Table 4.7 Chemical composition of return fine (wt%)

Composition	Fe _{total}	FeO	Ni	CaO	MgO	Al ₂ O ₃	SiO ₂	Loss on ignition
Content	26.18	12.64	2.14	2.12	16.11	4.44	31.43	0.68

Table 4.8 Particle size distribution of return fine (wt%)

Size	5–3 mm	3–1 mm	1–0.25 mm	<0.25 mm
Proportion	58.27	23.25	6.70	11.96

4.5.1.2 Sintering Pot Test Procedure

The sintering pot test procedure included proportioning, mixing, granulation, ignition, sintering, cooling and sieving. The mixture of raw materials for sintering pot test consisted of 25 wt% return fine, 12 wt% coke breeze, and 35 wt% moisture. Besides, the quick lime dosage was determined by quaternary basicity of the mixture. The raw materials were proportioned and mixed manually, and then the mixture was charged into a granulator drum (diameter of 600 and length of 250 mm) for granulation at 15 rpm for 4 min. 200 g of sinter with particle size of 10–16 mm was filled in the pot bed, followed by charging the granulated mixture into a sinter pot (diameter of 100 mm and length of 500 mm). The total load height was 500 mm. Natural gas was used for ignition at 1150 °C for 2 min under a suction pressure of 5 kPa. After ignition, air was sucked into the mixture bed, and sintering was carried out at a suction pressure of 10 kPa, followed by cooling for 3 min at a suction pressure of 5 kPa. The cooled sinter was shattered four times from 2 m height and screened with a series of sieves with pore sizes of 5 × 5 mm, 10 × 10 mm, 16 × 16 mm, 25 × 25 mm and 40 × 40 mm, respectively. The sinter weight of various particle sizes was measured.

The properties of sinters produced in the pot were examined by determination of vertical sintering velocity (VSV), yield (Y), productivity (P) and ISO tumbling index (TI).

- (1) Vertical sintering velocity (VSV, mm/min):

$$VSV = H/t \quad (4.3)$$

where H is the height of sintering bed, mm, and t is the sintering time (the total time from the ignition to the sintering end point), min.

- (2) Yield (Y , %):

$$Y = (m_1 - 0.2)/(m_0 - 0.2) \times 100\% \quad (4.4)$$

where m_0 is the weight of total sinter, kg; m_1 is the weight of sinter oversize of 5 × 5 mm, kg, and 0.2 is the weight of hearth sinter, kg.

- (3) Productivity (P , t/m²·h):

$$P = 7.65 \times 10^4 m_0 / D^2 \cdot t \quad (4.5)$$

where D is the diameter of sinter pot, mm.

(4) 1/5 ISO tumbling index (TI , %):

$$TI = m'_1/3 \times 100\% \tag{4.6}$$

where the coefficient 3 is the weight of test sinters with the size of 10–40 mm, kg, and m'_1 is the weight of sample over size of 6.3×6.3 mm aperture after tumbling, kg.

4.5.1.3 Sintering Pot Tests for Saprolitic Laterite Ore

The variations of sintering properties with quaternary basicity in the range 0.5–2.0 are shown in Fig. 4.40. The indexes, VSV , Y and P , firstly increased and then decreased with increasing quaternary basicity, but the TI index decreased constantly. Due to the high moisture content of mixture and shrinkage in the sintering process, there were many hollow channels in the middle of the sintering cup. As a result, the sintering speed was fast. However, as more diopside was formed at the quaternary basicity of 0.8–1.2, the assimilation performance of diopside was better than that of olivine, so the sintering speed was faster at the quaternary basicity of 0.8–1.2.

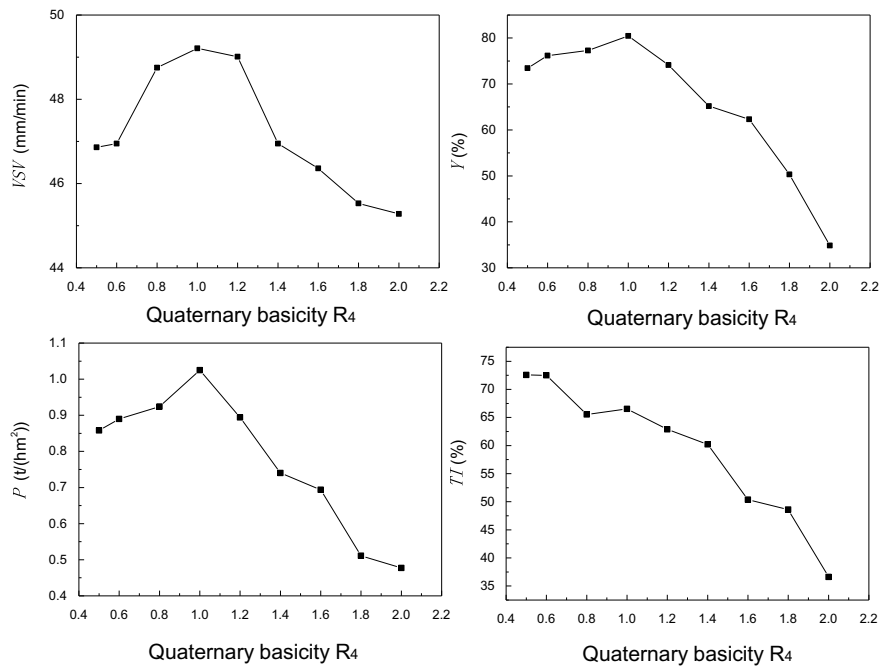


Fig. 4.40 Effect of quaternary basicity on the sintering properties of saprolitic laterite ore

With the quaternary basicity varying from 0.5 to 1.0, Y and P values increased from 72.43% to 80.46% and from 0.85 t/(h·m²) to 1.0 t/(h·m²), respectively. The other index TI , however, declined gradually as the basicity increased. Its value decreased from 72.6% to 66.5% when the basicity increased from 0.5 to 1.0. The results of sintering indexes showed that selecting an appropriate quaternary basicity was of significance for enhancing strength and productivity of sinters of saprolitic laterite ore. Although TI kept decreasing with increasing basicity, its value still met the requirement ($TI \geq 70\%$ in actual production process and one could just ensure if TI is above 60% in the laboratory test) of small blast furnace (volume: 400–600 m³).

4.5.1.4 Phase Composition of Saprolitic Laterite Ore Sinters

The phase composition of the sinter can reflect the composition of the binding phase. Figure 4.41 shows the XRD patterns of the saprolitic laterite ore sinters with different quaternary basicities. The sinter with natural quaternary basicity of 0.5 was mainly composed of olivine, enstatite and spinel. With the increase of the quaternary basicity, the binding phase composition of the sinter was similar. It was composed of olivine, diopside and monticellite. Other phases with high melting point, such as akermanite, merwinite and calcium silicate, failed to form the binding phase and entered the return fine after sintering. The results of XRD quantitative analysis of the binding phases of the sinters are shown in Fig. 4.42. Olivine was the main binding phase in the sinter with natural basicity due to the high coke addition of 12 wt%. When the basicity increased to 1.0, the content of olivine decreased and enstatite disappeared. Instead, monticellite and diopside with low melting point were generated. In general, these transformations could improve sinter properties.

4.5.1.5 Microstructures of Saprolitic Laterite Ore Sinters

Figure 4.43 shows the optical micrographs of the sinters with natural basicity of 0.5 and quaternary basicity of 1.0. It was seen from Fig. 4.43a that the sinter with natural basicity comprised olivine, enstatite and spinel. Finely crystallized olivine and spinel were embedded in enstatite. Because of the reducing atmosphere, Fe³⁺ ions were reduced to Fe²⁺ ions with decreased content of magnesium in the spinel and increased iron hosted in the enstatite, as shown in Fig. 4.44. With the quaternary basicity of 1.0, the composite binding phases in the sinter consisted of olivine, diopside, and monticellite. The structure of spinel was partially destroyed (Fig. 4.43b). Besides, as shown in Fig. 4.43b, there were some pores in the sinter with the quaternary basicity of 1.0, due to the formation of liquid phase.

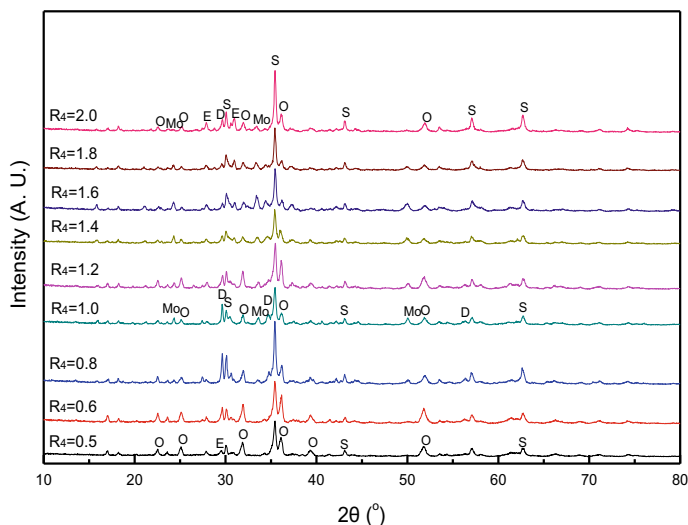


Fig. 4.41 XRD patterns of saprolitic laterite ore sinters with different quaternary basicities. (*D* diopside $\text{CaMgSi}_2\text{O}_6$; *E* enstatite MgSiO_3 ; *Mo* monticellite CaMgSiO_4 ; *O* olivine $(\text{Mg}, \text{Fe})_2\text{SiO}_4$; *S* spinel MgFe_2O_4)

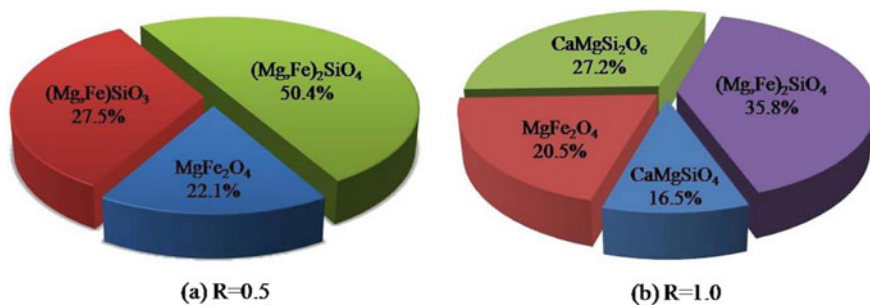


Fig. 4.42 Phase compositions of saprolitic laterite ore sinters with different quaternary basicities, reprinted from Ref. [11], copyright 2022, with permission from Springer Nature

4.5.1.6 Metallurgical Properties of Saprolitic Laterite Ore Sint

The metallurgical properties of sinter, including the low temperature reduction degradation, reducibility and softening-melting and dripping properties, were measured. Figure 4.45 shows the results of low temperature reduction degradation ($\text{RDI}_{+3.15}$) and reduction degree of saprolitic laterite ore sinters with quaternary basicities of 0.5 and 1.0. The low temperature reduction degradation of sinters exceeded 95%, while the value at the quaternary basicity of 1.0 was slightly higher than that at the natural basicity of 0.5. These results showed that the two types of sinter would not pulverize during the reduction process, which guaranteed the reduction strength of

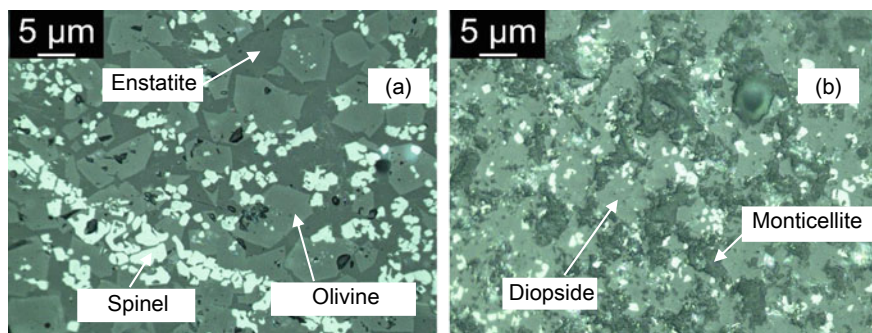


Fig. 4.43 Microstructures of saprolitic laterite ore sinters with different quaternary basicities. **a** $R_4 = 0.5$ and **b** $R_4 = 1.0$, reprinted from Ref. [11], copyright 2022, with permission from Springer Nature

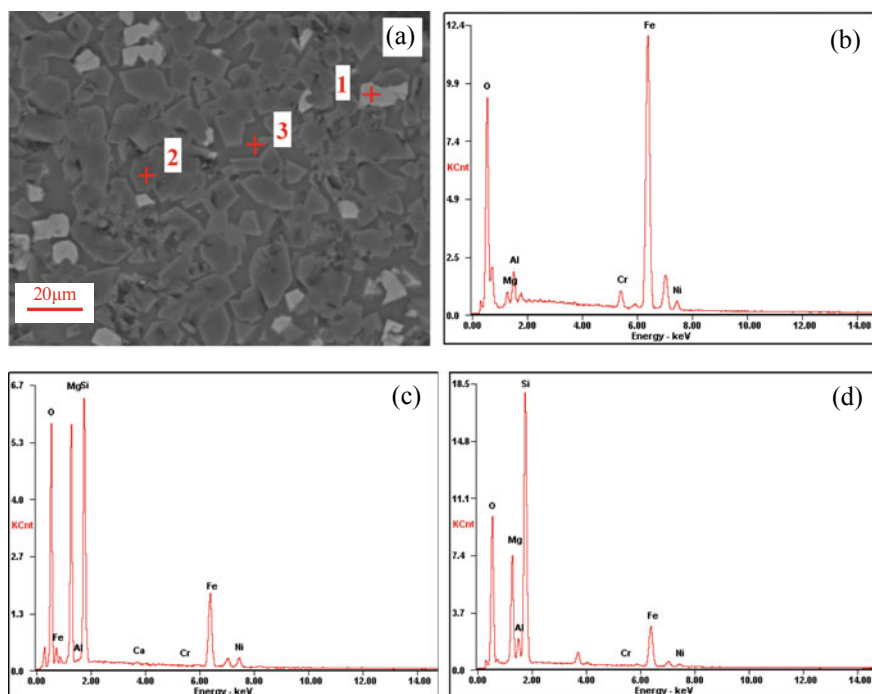


Fig. 4.44 SEM-EDS analyses of the saprolitic laterite ore sinter with natural basicity. **a** backscattered electron image, **b** EDS spectrum of spot 1, **c** EDS spectrum of spot 2, and **d** EDS spectrum of spot 3, reprinted from Ref. [11], copyright 2022, with permission from Springer Nature

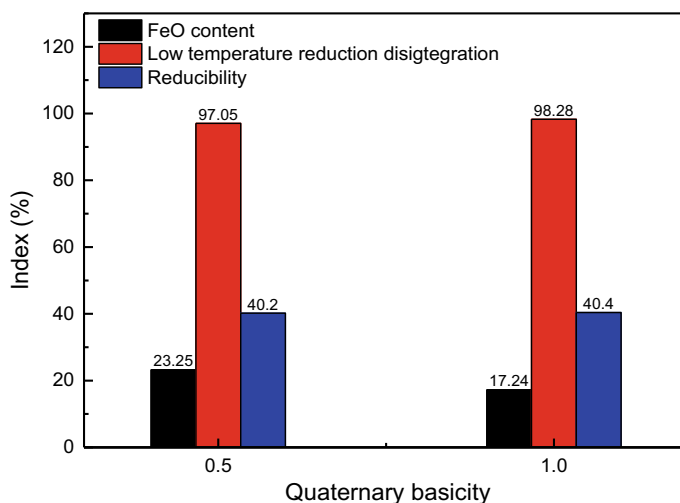


Fig. 4.45 Low temperature reduction disintegration and reducibility of saprolitic laterite ore sinters

sinter during blast furnace smelting. The reduction degrees of the two sinters were relatively low, namely 40.2% and 40.4%, respectively. The results of chemical titration showed that the contents of ferrous oxide in the sinter with quaternary basicities of 0.5 and 1.0 were 23.25 wt% and 17.24 wt%, respectively. The high carbon content of the mixture of raw materials for sintering led to higher content of ferrous oxide in the sinter and to lower reduction degree of the sinter.

Table 4.9 shows the softening–melting and dripping properties of sinters with different quaternary basicities. When the quaternary basicity was 1.0, the liquid dripping temperature was lower than that at the natural basicity of 0.5. In particular, the liquid dripping temperature of sinter with quaternary basicity of 1.0 was only 1113 °C, which was decreased by 84 °C compared with the sinter having quaternary basicity of 0.5.

The low softening beginning and ending temperatures indicate that the sinter will melt at a low smelting temperature, which is conducive to reducing the coke

Table 4.9 Softening–melting and dripping properties of saprolitic laterite ore sinters

Property	$R_4 = 0.5$	$R_4 = 1.0$
Softening beginning temperature, T_a (°C)	1024	1008
Softening ending temperature, T_s (°C)	1103	1073
Bed pressure sudden rising temperature, T_m (°C)	1134	1087
Liquid dripping temperature, T_d (°C)	1197	1113
Softening temperature range, $(T_s - T_a)/^{\circ}\text{C}$	79	65
Melting temperature range, $(T_d - T_m)/^{\circ}\text{C}$	63	26

addition and energy-saving production in the blast furnace. The low dripping temperature shows the low slag viscosity, which is of great significance to the separation of slag and molten iron. In addition, the narrow softening and melting zone can reduce the resistance of softening-melting zone to gas and improve the permeability of blast furnace charge. For the small blast furnace of 300–600 m³ used in the smelting of laterite ore, the requirements for permeability and dripping temperature are relatively low. In view of this fact, the metallurgical properties of saprolitic laterite ore sinter can be improved with the quaternary basicity of 1.0.

4.5.2 Sintering of Limonitic Laterite Ore

4.5.2.1 Raw Materials

The typical limonitic laterite ores were taken from Indonesia. The ores were mixed with a certain amount of quick lime for drying in advance and the moisture contents of limonite-A and limonite-B were 20.50 wt% and 24.79 wt%, respectively. The main phases of laterite ores were goethite and chromite (Fig. 4.46). As shown in Table 4.10, the limonitic laterite ores were characterized by high iron content and low nickel content. The contents of total iron and nickel were nearly 48 wt% and 0.54 wt%, respectively. Besides, there were different contents of SiO₂, Al₂O₃, CaO, and MgO in both ores. The Al₂O₃ content in limonite-A was 6.62 wt%, which was higher than that of limonite-B. The limonite-B was featured by high Cr₂O₃ content

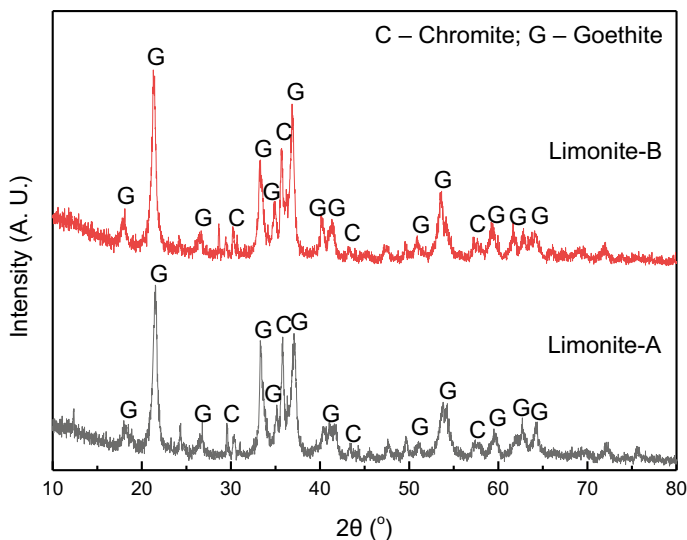


Fig. 4.46 XRD patterns of limonitic laterite ores

Table 4.10 Chemical compositions of limonitic laterite ores (wt%)

Limonite	Fe _{total}	Ni	Cr ₂ O ₃	MnO	CaO	SiO ₂	MgO	Al ₂ O ₃	Moisture
A	47.88	0.53	3.33	0.69	4.66	1.66	0.58	6.62	20.50
B	47.72	0.54	5.64	0.65	3.34	2.79	1.65	3.98	24.79

Table 4.11 Particle size distributions of limonitic laterite ores (wt%)

Size	+8 mm	8–5 mm	5–3 mm	3–1 mm	– 1 mm
Limonite–A	10.68	8.22	4.97	28.85	47.27
Limonite–B	14.32	11.42	8.50	19.52	46.25

of 5.64 wt%. The particle size distributions of the limonitic laterite ores are listed in Table 4.11. Approximately 46–47 wt% of the ore particles were smaller than 1 mm.

The mixture of coke breeze and anthracite with a given mass proportion was used as fuel in the sintering pot tests. Table 4.12 shows their proximate analyses. The fixed carbon contents of coke breeze and anthracite were 79.3 wt% and 82.8 wt%, respectively.

Quick lime and dolomite were used as fluxes. As shown in Table 4.13, the CaO contents in quick lime and dolomite were 79.1 wt% and 31.9 wt%, respectively. Besides, the MgO content in dolomite was 19.7 wt%. Dolomite was used to adjust the MgO content of sinter.

The return fine was produced from limonitic laterite ore. It was crushed to the particle size less than 5 mm. Its chemical composition is shown in Table 4.14.

Table 4.12 Proximate analyses of fuels and their ash compositions (wt%)

Fuel	Proximate analysis				Chemical compositions of ash				
	F _{cad}	V _{daf}	A _d	M _{ad}	TFe	SiO ₂	CaO	Al ₂ O ₃	MgO
Coke	79.3	2.6	17.0	1.1	8.0	48.4	5.2	28.4	2.5
Anthracite	82.8	5.2	11.1	0.9	6.6	52.5	1.4	24.1	1.3

F_{cad} fixed carbon content; V_{daf} volatile matter content; A_d ash content; M_{ad} moisture

Table 4.13 Chemical compositions of fluxes (wt%)

Flux	Fe _{total}	CaO	MgO	Al ₂ O ₃	SiO ₂	Loss on ignition
Dolomite	0.4	31.9	19.7	0.3	0.7	45.7
Quick lime	0.4	79.1	3.4	2.1	4.6	6.5

Table 4.14 Chemical composition of return fine (wt%)

Component	Fe _{total}	Ni	Cr ₂ O ₃	CaO	MgO	Al ₂ O ₃	SiO ₂
Content	52.0	0.9	2.4	8.5	3.3	5.3	5.9

4.5.2.2 Sintering Pot Tests for Limonitic Laterite Ore

The mixture of raw materials for sintering consisted of 35 wt% return fine, 1.7 wt% coke breeze, 5.0 wt% of anthracite, and 19 wt% moisture. Besides, the quick lime and dolomite dosages were determined by basicity of the mixture. The raw materials were proportioned and mixed manually, and then the mixture was charged into a granulator drum (diameter of 600 and length of 1400 mm) for granulation at 15 rpm for 5 min. 1.0 kg of sinter with particle size of 10–16 mm was filled in the pot bed, followed by charging the granulated mixture into a sinter pot (diameter of 180 mm and length of 900 mm). The total load height was 890 mm. Natural gas was used for ignition at 1100 °C for 3 min at the suction pressure of 8–9 kPa. After ignition, air was sucked into the mixture bed at the suction pressure of 10–11 kPa, followed by cooling for 3 min at the suction pressure of 5 kPa.

With the given binary basicity of 1.3, the sintering properties of limonitic laterite ore are shown in Table 4.15. The vertical sintering velocity of sintering mixture exceeded 31 mm/min. In other words, the sintering time did not exceed 29 min when the total load height was 890 mm. High Al_2O_3 content increased sintering velocity. With the Al_2O_3 content of 6.0 wt% and SiO_2 content of 5.5 wt%, the vertical sintering velocity of sintering mixture reached 49.95 mm/min, resulting in the maximum productivity of 2.69 $\text{t/m}^2\cdot\text{h}$. As shown in Table 4.15, with the Al_2O_3 content of 5.0 wt%, the yield and productivity of sinter increased with SiO_2 content from 5.5 wt% to 6.5 wt%. When the Al_2O_3 content was 5.5 wt% or 6.0 wt%, the yield of sinter reached the maximum value with the SiO_2 content of 6.0 wt%. However, the ISO tumbling index of sinters remained poor. The maximum TI value was only 56.67% with the Al_2O_3 content of 5.5 wt% and SiO_2 content of 6.5 wt%.

Table 4.15 Sintering properties of limonitic laterite ore

No	Variable conditions				Sintering properties			
	Al_2O_3 (wt%)	SiO_2 (wt%)	Binary basicity, R_2	Quaternary basicity, R_4	VSV, (mm/min)	Y , (%)	TI , (%)	P , ($\text{t/m}^2\cdot\text{h}$)
1	5.0	5.5	1.3	0.97	32.32	56.86	44.15	1.76
2		6.0		1.03	34.48	67.73	46.61	1.81
3		6.5		1.07	34.47	68.43	49.49	1.88
4	5.5	5.5	1.3	0.92	31.62	70.41	50.91	1.71
5		6.0		0.98	34.70	71.68	50.15	1.91
6		6.5		1.03	32.36	69.21	56.67	1.86
7	6.0	5.5	1.3	0.88	49.95	70.36	49.73	2.69
8		6.0		0.93	43.99	70.66	54.64	2.30
9		6.5		0.98	38.47	68.91	51.54	2.22

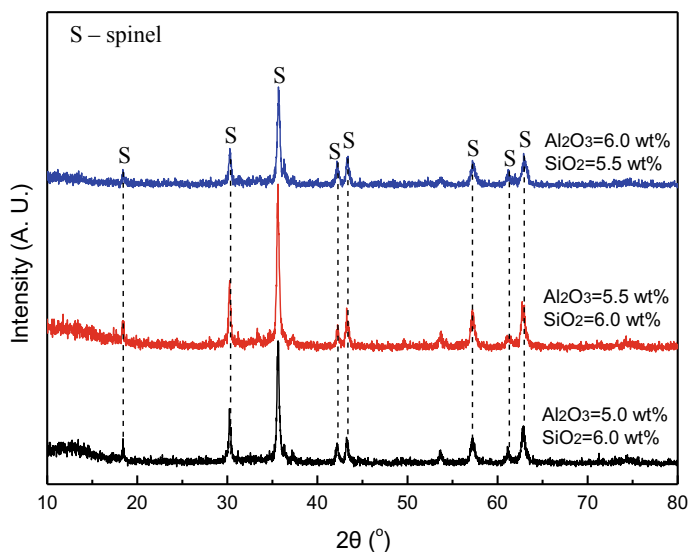


Fig. 4.47 XRD patterns of limonitic laterite ore sinters

4.5.2.3 Phase Composition of Limonitic Laterite Ore Sinters

Figure 4.47 shows the XRD patterns of limonitic laterite ore sinters. The main phase was spinel in the sinters with various Al_2O_3 and SiO_2 contents, which was different from saprolitic laterite ore sinters (Fig. 4.41). As shown in Fig. 4.48, the spinel was the unmelted phase in the sinters and most of the iron components occurred in spinel (Table 4.16). Besides, all aluminum and chromium components were present in spinel. This result confirmed that the aluminum component did not participate in the formation of binding phase. The binding phase consisted of iron, calcium, magnesium and silicon components (Table 4.16). However, due to its amorphous feature, it was not detected by XRD.

4.5.2.4 Metallurgical Properties of Limonitic Laterite Ore Sinters

Figure 4.49 shows the results of the low temperature reduction degradation ($\text{RDI}_{+3.15}$) and reducibility of limonitic laterite ore sinters. There was no obvious difference in the low temperature reduction degradation and reducibility in these two kinds of sinters and the low temperature reduction degradation exceeded 95%. The results showed that the two types of sinter would not pulverize during the reduction process, ensuring the reduction strength of sinter during smelting. Due to the difference in the ferrous oxide content, the reduction degrees of limonitic laterite ore sinters were 73.86% and 75.39%, respectively. Although their ferrous oxide contents were similar (Fig. 4.45), the reduction degree of limonitic laterite ore sinters was increased by

Fig. 4.48 SEM image of limonitic laterite ore sinter with the contents of 5.0 wt% Al_2O_3 and 6.0 wt% SiO_2

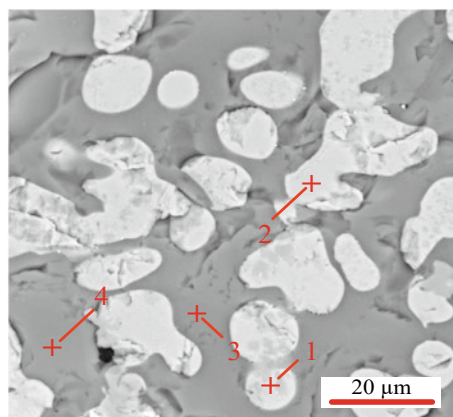


Table 4.16 EDS results of limonitic laterite ore sinter with 5.0 wt% of Al_2O_3 and 6.0 wt% of SiO_2

Spot	Element	O	Fe	Mn	Ca	Mg	Ni	Si	Al	Cr
1	wt%	26.93	62.22	0.82	0.53	1.88	0.98	0.00	4.00	2.17
	at%	53.96	35.71	0.48	0.42	2.48	0.54	0.00	4.75	1.34
2	wt%	24.16	69.05	0.87	0.51	4.89	0.00	0.00	0.51	0.51
	at%	50.57	41.40	0.53	0.42	6.74	0.00	0.00	0.33	0.33
3	wt%	39.86	12.51	0.69	22.87	7.62	0.00	16.44	0.00	0.00
	at%	59.36	5.34	0.30	13.59	7.47	0.00	13.94	0.00	0.00
4	wt%	37.57	13.99	0.57	24.25	7.29	0.00	16.32	0.00	0.00
	at%	57.34	6.12	0.25	14.77	7.33	0.00	14.19	0.00	0.00

nearly 35% compared with the saprolitic laterite ore sinters. It was attributed to the high total iron content in the limonitic laterite ore (Tables 4.1 and 4.10).

Table 4.17 shows the softening-melting and dripping properties of limonitic laterite ore sinters. With the Al_2O_3 content of 5.5 wt%, the properties of limonitic laterite ore sinters were very close to those with the SiO_2 contents of 5.5 wt% and 6.0 wt%. However, these characteristic softening and melting temperatures of limonitic laterite ore sinter were 200 °C higher than those of saprolitic laterite ore sinter with the quaternary basicity of 1.0 (Table 4.9). With the Al_2O_3 content of 5.5 wt% and SiO_2 content of 6.0 wt% (quaternary basicity of 0.98, as shown in Table 4.15), the softening beginning and ending temperatures of limonitic laterite ore sinter were 1208 °C and 1274 °C, respectively. Particularly, the liquid dripping temperature reached 1375 °C (Table 4.17), which was 262 °C higher than that of saprolitic laterite ore sinter. As a result, the required temperature of limonitic laterite ore sinter was high than that of saprolitic laterite ore sinter during the blast furnace smelting.

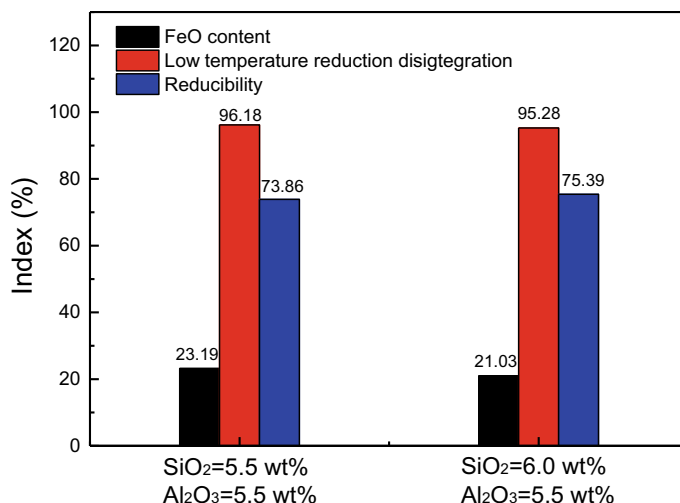


Fig. 4.49 Low temperature reduction disintegration and reducibility of limonitic laterite ore sinters

Table 4.17 Softening-melting and dropping properties of limonitic laterite ore sinters

Property	SiO ₂ = 5.5 wt% Al ₂ O ₃ = 5.5 wt%	SiO ₂ = 6.0 wt% Al ₂ O ₃ = 5.5 wt%
Softening beginning temperature, Ta (°C)	1206	1208
Softening ending temperature, Ts (°C)	1271	1274
Bed pressure sudden rising temperature, ΔTm (°C)	1309	1299
Liquid dripping temperature, Td (°C)	1381	1375
Softening temperature range, (Ts–Ta) (°C)	65	66
Melting temperature range, (Td–Tm) (°C)	72	76

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Chapter 5

Valorization of Ferronickel Slag for Preparation of Value-Added Materials



Abstract Along with the production of ferronickel from laterite ores, there are a large quantity of ferronickel slags, especially that from the RKEF process, which not only poses a potential hazard to environment but also represents a waste of the resource. By now, the slags have been used for production of building materials, preparation of functional materials, and recovery of valuable metals. Based on a summary of the current status of utilization of ferronickel slag, this chapter provides recent advances in using the slag for producing refractory materials and lightweight thermal insulation materials, covering thermodynamic analysis, experimental exploration, and production verification.

Keyword Ferronickel slag · Value-added utilization · Refractory materials · Thermal insulation materials

Production of ferronickel from saprolitic laterite ores by the RKEF process has undergone rapid development around the world. The RKEF process has become the mainstream process of ferronickel production. About 90% of ferronickel in China is produced by this process, which supports the rapid development of China's stainless-steel industry in the past decade. However, because of the very low percentage of nickel in the natural ores (1–2 wt%), a significant quantity of slag is generated during the production of ferronickel. It was estimated that approximately 4–6 tons of ferronickel slag are generated in the production of 1 ton of ferronickel [1]. At present, however, less than 10 wt% of ferronickel slag is utilized and most of ferronickel slag is disposed in an open environment [1]. According to incomplete statistics, the cumulative stock of ferronickel slag in China is more than 200 million tons and it is still increasing at a rate of about 40 million tons per year [2, 3]. The massive stacking of ferronickel slag poses a great threat to ground and underground water due to its high contents of hazardous elements, including 1.08–3.07 wt% chromium oxide.

Currently, China has put environmental protection work to an unprecedented height, which has brought enormous environmental protection pressure to ferronickel

production enterprises. The ferronickel slag disposal seriously threatens the sustainable development of ferronickel and stainless-steel industry. The utilization of ferronickel slag is extremely important for sustainable development of the industry.

Based on the basic properties of ferronickel slag, the methods for utilization of the slag with their advantages and disadvantages were explored in this chapter. A focus was put on preparing refractory materials and high temperature lightweight thermal insulation materials from ferronickel slag.

5.1 Properties of Ferronickel Slag

Ferronickel slag is produced as a byproduct from ferronickel smelters. Due to the different raw materials processed, the chemical compositions of the slags produced by different smelting processes were also significantly different. The slags can be roughly divided into three types, namely rotary kiln ferronickel slag, blast furnace ferronickel slag and electric furnace ferronickel slag. Their main chemical compositions are shown in Table 5.1. The total content of magnesium oxide and silicon oxide in the rotary kiln ferronickel slag and electric furnace ferronickel slag is about 80% and the total content of calcium oxide and aluminum oxide in the blast furnace ferronickel slag is much higher than those of the rotary kiln ferronickel slag and electric furnace ferronickel slag. The X-ray diffraction (XRD) patterns of these slags are shown in Fig. 5.1. The rotary kiln ferronickel slag is mainly composed of olivine, enstatite, and forsterite. The blast furnace ferronickel slag is mainly composed of magnesium aluminate spinel. The electric furnace ferronickel slag is mainly constituted by olivine.

Table 5.1 Main compositions of typical ferronickel slags (wt%)

Slag*	SiO ₂	MgO	FeO	Al ₂ O ₃	CaO	Cr ₂ O ₃	NiO
Rotary kiln ferronickel slag	53.40	28.40	7.14	2.50	5.70	0.90	0.20
Blast furnace ferronickel slag	30.54	12.47	1.54	26.74	21.61	1.78	0.01
Electric furnace ferronickel slag	48.29	30.95	7.39	4.04	2.40	2.11	0.06

*Notes Rotary kiln ferronickel slag and blast furnace ferronickel slag were obtained from Beihai Chengde Nickel Industry Co., Ltd. Electric furnace ferronickel slag was obtained from Guangdong Guangqing Metals Technology Co., Ltd

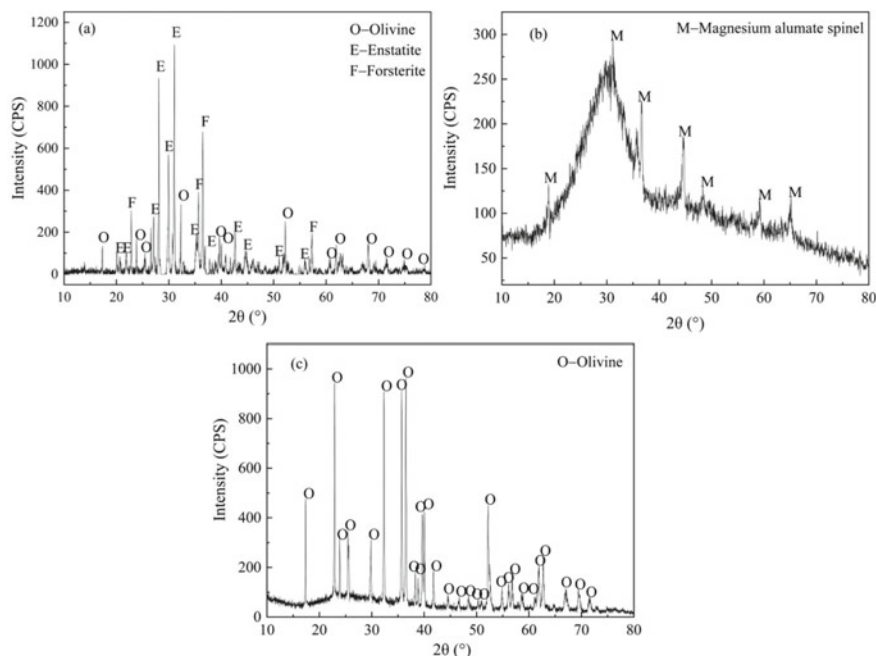


Fig. 5.1 XRD patterns of ferronickel slags (**a** Rotary kiln ferronickel slag, **b** Blast furnace ferronickel slag, and **c** Electric furnace ferronickel slag)

5.2 Current Status of Utilization of Ferronickel Slag

Compared with ordinary slags in ferrous metallurgy, ferronickel slag has more complex chemical components, featured by high contents of magnesium oxide and silicon oxide. It also contains ferrous oxide, aluminum oxide and a small amount of harmful heavy metal elements, such as Cr. At present, the methods of ferronickel slag utilization mainly include production of building materials, preparation of functional materials, and recovery of valuable metals.

5.2.1 Production of Building Materials

Ferronickel slag is obtained after smelting at temperature of about 1600 °C. It has certain corrosion resistance and stability, exhibiting a potential in the application of reclamation materials with high anti-corrosion requirements. It can also be used as a good roadbed filling material and railway roadbed material. Because ferronickel slag has certain cementation activity, it may be used as filling material, cement, concrete admixture, etc.

In the 1990s, Japan successfully used ferronickel slag as concrete aggregates and admixtures. In Greece, many studies were reported for treatment of ferronickel slag, including using ferronickel slag as cement admixture, concrete aggregates, and raw materials of ceramsite and geopolymers. Also, the slag was used for production of high-aluminum cement. In the United States, the slowly-cooled ferronickel slag with Moh's hardness of 5 to 6 was used as a concrete admixture for asphalt pavement after being thermally mixed with asphalt. When the gas-cooled ferronickel slag with good stability is used as the coarse and fine aggregates of hot asphalt, the adaptability of the asphalt to the environment could be improved. For the use in preparing roadbed filling materials, it has the advantages of rapid disposal of the waste, despite low economic value [1, 4].

In China, in the field of replacing some natural sand with ferronickel slag, it was shown that the slag after crushing and sieving met the requirements of various indexes of construction sand. There was little difference between performance of the concrete and ordinary natural sand concrete. The study of the effect of ferronickel slag on the working performance, compressive strength, tensile bond strength and linear expansion rate of mortar after replacing the river sand with different amounts of ferronickel slag also indicated that the replacement of river sand by ferronickel slag could improve the mortar flow and reduce the stratification of the mortar, finally improving the working performance [5]. When the substitution percentage of ferronickel slag was less than 80%, the compressive strength of the mortar increased with the substitution percentage. When all the river sand was replaced, the compressive strength of the mortar would be reduced compared with that with substitution percentage of 80%. The smoothness of mortar surface tended to deteriorate after the substitution percentage of ferronickel slag exceeded 60%. The tensile bond strength reached the highest value of 0.41 MPa when the substitution percentage of ferronickel slag was 40%. However, because the slag has a certain alkali-aggregate reaction hazard, the substitution of ferronickel slag should not exceed 40% [5].

The low contents of calcium oxide and aluminum oxide, high content of silicon oxide, large silicon-oxygen polymerization degree, and low activity index (less than 50%) result in weak gelation of ferronickel slag. The key to use of ferronickel slag as a raw material for producing building materials is to solve the problem of low activity of ferronickel slag. The gelation activity of ferronickel slag can be improved by mechanical activation and chemical excitation. Mechanical activation is usually achieved by grinding ferronickel slag to improve its activity, with a target to specific surface area of the slag more than 6000 cm²/g. When the slag was crushed and ground to the same fineness as the cement clinker and the content of ferronickel slag was 25%, the indexes could meet the relevant requirements of PO32.5 cement, but the activity index did not reach the index of granulated blast furnace slag powder listed in the Chinese National Standard Test Method, namely GB/T18046-2008 [6, 7].

In addition, ferronickel slag has high contents of silicon oxide and iron oxide, and can replace part of clay and iron powder as raw materials for preparing cement clinker. It was successful to replace the original clay-iron ore ingredients with wet fly ash and ferronickel slag and to use oil shale slag as mineral admixture to produce PC32.5R composite Portland cement and PO32.5R ordinary Portland cement, and

cement with PO42.5 or above [8]. However, due to the high content of magnesium oxide in the slag, it will adversely affect the stability of the cement and it is necessary to strictly control the addition of ferronickel slag. The amount of ferronickel slag blended in the cement production batch is up to 10%. Using ferronickel slag not only improves calcination, but also promotes the quality of cement clinker.

Like metallurgical slags such as steel slag, ferronickel slag can also be used as concrete admixture. The ferronickel slag-based auxiliary cementing material has many benefits, such as water reduction, plasticization, reinforcement, shrinkage reduction, and carbonation resistance. With a proper dosage, the work performance is improved significantly. After mixing metallurgical slags, such as ferronickel slag and steel slag, with appropriate amount of activator (gypsum or water glass) and crushing and grinding to a fineness of 400–800 m²/kg, the strength and work performance of concrete could be significantly improved by replacing 10%–30% cement under the same conditions [9]. The slump value of the concrete mixture was increased and the loss over time was reduced. The suitable amount of ferronickel slag to replace cement in concrete was found to be 15%.

In addition to being used in cement and concrete, ferronickel slag has been used to produce building blocks. By using fine ferronickel slag as cementing material, crushed ferronickel slag as aggregates, sodium silicate as alkali activator, and other additives for adjusting contents of calcium oxide and aluminum oxide, the compressive strength of the resulting building block could reach 28.9 MPa. At this moment, the addition of ferronickel slag was as high as 94% [10, 11]. In addition, it was found that the strength of the building block produced by using the crushed ferronickel slag as the aggregate was higher than that of the river sand as the aggregate. There were unsaturated Si–O bonds and Al–O bonds and an activation reaction could also occur under the action of an alkaline solution to form an octagonal-type hydrated sodium aluminosilicate and a calcium zeolite-type hydrated calcium aluminosilicate. Thereby, the overall strength of the building block was improved. Under the conditions of the tailings to ferronickel slag ratio of 1, the additions of cement and chemical activators (NS and CA) of 20% and 2.5%, respectively, the water-to-binder ratio of 0.5, a baking-free brick whose performance met the requirements of MU25 in JC 422–2007 could be obtained by pouring molding, following by low-temperature curing [12].

The fly ash and ferronickel slag can be used as raw materials for producing geopolymers under the action of alkali activators, such as sodium silicate and sodium hydroxide. The geopolymer prepared from ferronickel slag had compressive strength of 110.32 MPa after 28 days, and excellent thermal stability and durability. The mass loss percentage of the prepared geopolymer in 30 freeze–thaw cycles was less than 2% and its compressive strength was still up to 83.93 MPa. When the fly ash addition reached 50%, the compressive strength of the fly ash-ferronickel slag geopolymer after 28 days was 71.83 MPa, decreased by 33.0% compared with that without the addition of fly ash, but still much higher than the fly ash geopolymer. Meanwhile, the fly ash-ferronickel slag geopolymer with the addition of 50% ferronickel slag

had good thermal stability and durability after 30 freeze–thaw cycles. The mass loss percentage was less than 2%, with the compressive strength of 54.93 MPa [13–15].

5.2.2 Preparation of Functional Materials

According to the chemical composition and phase characteristics of ferronickel slag, it may be used for preparing functional materials. Many studies mainly focused on the use of ferronickel slag for preparation of glass–ceramics, inorganic mineral fibers, thermal insulation materials, etc. [16–27].

The production of glass–ceramics is a new method for efficient use of solid waste. Glass–ceramic is a kind of functional material containing a large amount of microcrystalline phase and glass phase obtained by controlling crystallization during heating using parent glass of a specific composition. Because of its excellent properties, it is widely used in construction, transportation, aviation, biology, electronics, defense, and other fields. In the late 1950s, slag-based glass–ceramics were successfully developed in the former Soviet Union and then the production of glass–ceramics developed rapidly.

The $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS)-based glass–ceramics have excellent bending, compression and impact resistance, good chemical stability, and strong wear resistance. They have been widely used as high-grade building decoration materials to replace natural granite and high-grade wall tiles. Because ferronickel slag has high contents of SiO_2 and MgO while fly ash has high contents of SiO_2 , Al_2O_3 , and CaO , their compositions are basically complementary. Therefore, ferronickel slag and fly ash could be synergistically used as the main materials to prepare CMAS-based glass–ceramics. For instance, a study reported the preparation of CMAS-based glass–ceramics using a mixture of 55% ferronickel slag and 45% fly ash [17]. Initially, the mixture was melted at 1550 °C and after being kept for 1 h it was poured into cold water for water quenching. Then, the water quenched slag was ground to –200 mesh to obtain a CMAS-based glass–ceramic parent material which was nucleated and sintered at 860 °C for 1 h and liquefied at 980 °C for 1.5 h. Lastly, a glass–ceramic with anorthosite and enstatite as the main phases and spinel as the minor phase was obtained. The glass–ceramic had high flexural strength (86.76 MPa) and low water absorption (0.09%). The results showed that it is feasible to prepare glass–ceramic by using ferronickel slag. However, the preparation process was long and the crystallization process is difficult to control. By now, no relevant industrial application has been reported.

Ferronickel slag, often containing 60%–65% ($\text{SiO}_2 + \text{Al}_2\text{O}_3$), has high cohesive properties at high temperature and good fiber-forming properties at smelting temperature (1500 °C–1600 °C). The slag fiber can be used as expansion joint filler for industrial furnace brick wall. The refractoriness of the fiber from ferronickel slag can reach 700 °C, which is higher than the blast furnace slag fiber by more than 100 °C. Meanwhile, the cost for producing ferronickel slag fibers is lower. In addition, the chemical stability of ferronickel slag fiber is better than that of the blast furnace

slag fiber in the corrosive medium. However, because of the chemical composition features of ferronickel slag, additives are usually required for the production process.

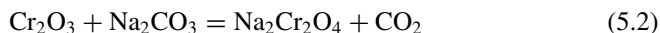
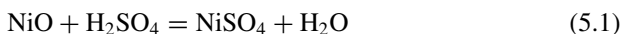
In recent years, there have been reports on the use of ferronickel slag to prepare inorganic mineral fibers in China. The main purpose is to use high-temperature (above 1600 °C) slag produced during smelting to produce ultra-fine inorganic mineral fibers using special facilities, such as high-speed centrifugal machine. The ultra-fine inorganic fibers (diameter of 3–6 μm and length of 30–90 μm) are softened, modified, and chemically treated. They are then used to replace plant fibers in papermaking and to produce thermal insulation materials and other building materials. The fibers prepared by this method often contain residual slag, with different diameters and lengths. Hence, these problems still need to be solved [19, 20].

Because the main phase of ferronickel slag is olivine ($2[(\text{Mg}, \text{Fe})\text{O}] \cdot \text{SiO}_2$), ferronickel slag has been used for producing lightweight thermal insulation materials, with the additions of magnesium oxide powder, magnesium carbonate powder, silicon powder, titanium dioxide powder, zirconia powder, and carbon black powder. After mixing at a suitable ratio, the mixture was kept at 500–700 °C for 4–8 h and then kept at 1300–1550 °C for 2–6 h. A forsterite-type lightweight thermal insulation material was produced with the bulk density of 1.55–1.75 g/cm³, compressive strength of 5.5–8.5 MPa, pore porosity of 77%–88% (<20 μm), and thermal conductivity at 1000 °C of 0.665–0.695 W/(m·K) [21]. The method made good use of the composition and phase characteristics of ferronickel slag and the addition of ferronickel slag could be up to 75%, which paves a new way for efficient utilization of ferronickel slag. However, compared with the requirements of common insulation materials, the lightweight insulation material does not have sufficiently low bulk density (the bulk density should generally be less than 1.3 g/cm³) which causes high thermal conductivity. In addition, multiple additives and long production time are required, leading to high energy consumption.

5.2.3 Recovery of Valuable Metals

The methods of recovering valuable metals from ferronickel slag mainly include the hydrometallurgical and pyrometallurgical processes. The hydrometallurgical processes use acid leaching or alkali fusion/leaching to dissolve nickel, cobalt, chromium, and other elements in the slag. Thereafter, the valuable components are separated and purified from the solution. The pyrometallurgical processes are used to selectively enrich valuable components, such as nickel, cobalt, iron, and magnesium, in the slag by roasting before their separation and recovery.

In order to recover nickel and cobalt from ferronickel slag, magnetic separation is used for preliminary enrichment of nickel in the magnetic material, while chromium is enriched in the non-magnetic material. Thereafter, nickel is extracted from the magnetic material by acid leaching, while chromium is recovered from non-magnetic material by alkali fusion. The mechanism is given by the following reactions.



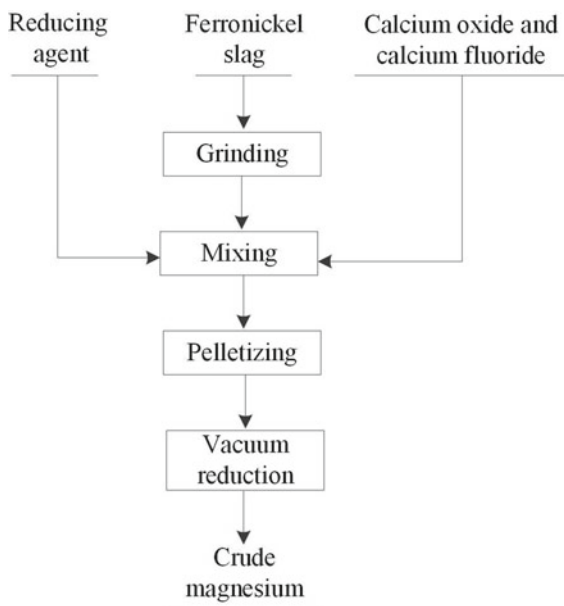
The acid leaching of nickel is to dissolve nickel oxide in the magnetic material in the acid, while the alkali leaching is to dissolve chromium oxide in the non-magnetic material to form sodium chromate, which is water soluble. The experimental results showed that after magnetic separation, nickel was enriched from 0.26% to 2.57% in the magnetic material, and chromium was enriched from 4.55% to 4.61% in the non-magnetic material. The leaching of nickel reached 91.5% under the conditions of sulfuric acid concentration of 220 g/L, leaching temperature of 110 °C, and leaching time of 2 h. Chromium was recovered from the non-magnetic material by sodium carbonate roasting-water leaching. The leaching of chromium reached 94.1% under the conditions of mass ratio of sodium carbonate to non-magnetic material of 0.65, roasting temperature of 1000 °C, and roasting time of 1 h. Another study reported recovery of nickel and cobalt from ferronickel slag by direct leaching using sulfuric acid under the optimal conditions. The leaching percentages of cobalt and nickel reached 77% and 35%, respectively [28–30].

Based on the mechanism of the Pidgeon process, magnesium can be extracted from ferronickel slag by vacuum reduction and the reduction reaction is shown by Eq. (5.3). The process of extracting magnesium from the slag by the Pidgeon method is shown in Fig. 5.2. When the aluminum–silicon–iron alloy was used as a reducing agent and 3% CaF_2 was added under the conditions of the system pressure of 1–5 Pa, reduction temperature of 1200 °C, and reduction time of 5 h, the reduction percentage of magnesium oxide in the slag was 46.82% [31].

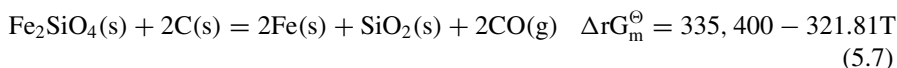
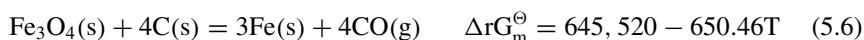
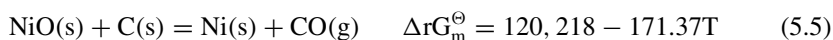


Gu et al. also evaluated the feasibility of recovering magnesium from ferronickel slag by vacuum reduction based on the thermodynamic analysis and experimental verification [32]. The thermodynamic calculations indicated that the magnesia in slag could be reduced to gaseous magnesium by Si, FeSi, Al, and C, with the minimum reduction temperatures of 2051, 2257, 1405, and 2307 °C at 100,000 Pa, respectively. As the system pressure decreased, the minimum reduction temperatures declined significantly. It was found that Si was suitable for recovery of magnesium from ferronickel slag with the minimum reduction temperature of 1312–1400 °C at 10–100 Pa despite stricter requirements for the addition of the reducing agent and temperature as the pressure decreased. For improving vacuum reduction, CaO was found to be a good additive for eliminating the negative impact of SiO_2 on the reduction. The experimental verification test showed that after vacuum reduction of ferronickel slag at 1300 °C for 3 h in the presence of 50 wt% Si and 30 wt% CaO at the pressure of 10 Pa, the recovery of Mg reached 97.74%, which was much higher than that without addition of CaO (35.73%). These results confirmed the good viability of recovering magnesium from ferronickel slag by vacuum reduction in the presence of CaO.

Fig. 5.2 Flowsheet of recovery of magnesium from ferronickel slag by the Pidgeon process



For recovery of nickel, copper and iron in the slag generated from smelting of nickel sulfide ore, a new selective reduction-magnetic separation method has been developed. The reaction mechanism is shown by Eqs. (5.4)–(5.7). The selective reduction of nickel, copper, and iron could be achieved by controlling the reduction temperature. It was reported that under the conditions of alkalinity of 0.15, coal dosage of 5%, reduction temperature of 1200 °C, reduction time of 20 min, and magnetic field strength of 131.34 kA/m, the nickel content in the magnetic concentrate was increased to 3.25 wt%. Meanwhile, the copper content was 1.20 wt% and the iron content was 75.26 wt% [33]. The recovery percentages of nickel, copper and iron were 82.20%, 80.00% and 42.17%, respectively.



The hydrometallurgical process has high acid consumption due to high magnesium and silicon contents in ferronickel slag. The composition of the ions entering

the solution during acid leaching is complicated, which adversely affects subsequent separation and purification of the valuable components. At the same time, the silica gel formed during the acid leaching process often causes large viscosity of the solution, and thus difficult solid–liquid separation. The silica gel is also easy to entrain other components and reduce the recovery percentage. Therefore, high recovery cost and difficult separation and purification limit the application of the hydrometallurgical technology.

Due to the low contents of nickel, cobalt and iron in ferronickel slag and the complicated relationship between them, the pyrometallurgy processes have the disadvantages of poor enrichment of valuable elements, low processing efficiency, and high comprehensive energy consumption.

In summary, due to the limitation by the characteristics of ferronickel slag, at present, only a small amount of ferronickel slag is consumed in production of underground filling cement, building materials, and synthetic geopolymers. The recycling of ferronickel slag still faces the challenges of low utilization percentage and efficiency, high production cost, and unsatisfied product quality. Therefore, it is essential to seek feasible and viable routes for treatment of ferronickel slag. The utilization of ferronickel slag for producing materials with good market prospect, no secondary pollution, and high added value deserves further study. As mentioned above, the chemical and phase compositions of ferronickel slag are complex. Compared with other methods, preparing refractory materials and lightweight thermal insulation materials from ferronickel slag has the advantages of high resource utilization ratio and great market prospect.

5.3 Preparation of Refractory Materials from Ferronickel Slag

5.3.1 Thermodynamic Analysis for Preparing Refractory Materials from Ferronickel Slag

The ferronickel slag generated from electric furnace has high contents of SiO_2 (40 wt%–50 wt%) and MgO (25 wt%–35 wt%), and certain amounts of FeO (5 wt%–10 wt%), Al_2O_3 (2 wt%–5 wt%), Cr_2O_3 (0.1 wt%–3 wt%). In general, its main phase is olivine. The main chemical and phase compositions of ferronickel slag are close to those of forsterite refractory materials. Thus, the thermodynamic characteristics of ferronickel slag sintered in the presence of magnesia (additive) for preparing refractory materials were assessed by thermodynamic calculations.

5.3.1.1 $\Delta_r G_m^\ominus$ - T Analysis

In the sintering process of ferronickel slag with the addition of magnesia, the variations of standard Gibbs free energy changes of reactions with temperature are shown in Table 5.2 and Fig. 5.3.

According to Table 5.2 and Fig. 5.3, the tendency of MgO to react with SiO₂ to form forsterite is stronger compared with the tendency to form enstatite at 1000–2000 °C. The generated enstatite can further react with MgO to form forsterite. However, when SiO₂ is excessive in the system, SiO₂ has reaction with the produced forsterite to form enstatite. At the same time, MgO can react with Al₂O₃, Fe₂O₃ and Cr₂O₃ in the system to form high melting point magnesium aluminate spinel (MgO·Al₂O₃, melting point of 2105 °C), magnesium ferrite spinel (MgO·Fe₂O₃, melting point of 1713 °C), and magnesium chromate spinel (MgO·Cr₂O₃, melting point of 2350 °C). The formation of spinel will increase the melting point of the system. In addition, CaO and Al₂O₃ in the system are easy to form high melting point calcium aluminate (1600 °C). Therefore, in order to ensure high refractoriness of the refractory material, it is necessary to add excessive MgO in the system.

Table 5.2 Variations of standard Gibbs free energy changes of reactions in the sintering process of ferronickel slag in the presence of magnesia with temperature

No.	Reaction	$\Delta_r G_m^\ominus = A + BT$, kJ/mol
5.8	$2\text{MgO} + \text{SiO}_2 = \text{Mg}_2\text{SiO}_4$	$-57.70 + 0.00008 T$
5.9	$\text{MgO} + \text{SiO}_2 = \text{MgSiO}_3$	$-8.64 + 0.0007 T$
5.10	$\text{MgSiO}_3 + \text{MgO} = \text{Mg}_2\text{SiO}_4$	$-6.49 + 0.00011 T$
5.11	$\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = 2\text{MgSiO}_3$	$-2.15 - 0.0018 T$
5.12	$\text{Mg}_2\text{SiO}_4 + 2\text{Al}_2\text{O}_3 = \text{MgO} \cdot \text{Al}_2\text{O}_3 + \text{MgSiO}_3$	$15.01 - 0.029 T$
5.13	$\text{Mg}_2\text{SiO}_4 + 2\text{Fe}_2\text{O}_3 = \text{MgO} \cdot \text{Fe}_2\text{O}_3 + \text{MgSiO}_3$	$-7.34 - 0.035 T$
5.14	$\text{Mg}_2\text{SiO}_4 + 2\text{Cr}_2\text{O}_3 = \text{MgO} \cdot \text{Cr}_2\text{O}_3 + \text{MgSiO}_3$	$-4.02 - 0.0067 T$
5.15	$\text{MgO} + \text{Al}_2\text{O}_3 = \text{MgO} \cdot \text{Al}_2\text{O}_3$	$-1.64 - 0.0013 T$
5.16	$\text{MgO} + \text{Cr}_2\text{O}_3 = \text{MgO} \cdot \text{Cr}_2\text{O}_3$	$-43.86 + 0.011 T$
5.17	$4\text{FeO} + \text{O}_2 = 2\text{Fe}_2\text{O}_3$	$-65.51 + 1.62 T$
5.18	$\text{MgO} + \text{Fe}_2\text{O}_3 = \text{MgO} \cdot \text{Fe}_2\text{O}_3$	$-9.65 + 0.0048 T$
5.19	$2\text{FeO} + \text{SiO}_2 = 2\text{FeO} \cdot \text{SiO}_2$	$-76.42 + 0.034 T$
5.20	$\text{FeO} + \text{SiO}_2 = \text{FeO} \cdot \text{SiO}_2$	$-8.04 + 0.0041 T$
5.21	$2\text{FeO} + \text{Al}_2\text{O}_3 = 2\text{FeO} \cdot \text{Al}_2\text{O}_3$	$-30.41 + 0.0096 T$
5.22	$\text{SiO}_2 + \text{Al}_2\text{O}_3 = \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	$-24.72 - 0.0021 T$
5.23	$\text{CaO} + \text{SiO}_2 = \text{CaO} \cdot \text{SiO}_2$	$-21.41 - 0.0002 T$
5.24	$3\text{CaO} + \text{Al}_2\text{O}_3 = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$-12.60 - 0.024 T$
5.25	$\text{CaO} + \text{Al}_2\text{O}_3 = \text{CaO} \cdot \text{Al}_2\text{O}_3$	$-18.00 - 0.019 T$
5.26	$\text{Mg}_2\text{SiO}_4 + 2\text{Al}_2\text{O}_3 + 4\text{SiO}_2 = 2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$	$-1.82 - 0.0047 T$

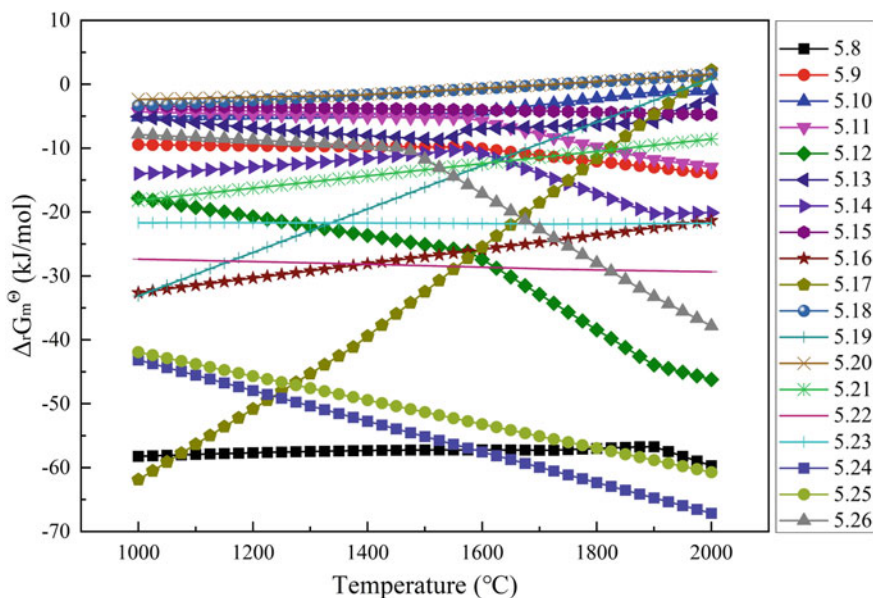


Fig. 5.3 $\Delta_r G_m^\ominus$ -T diagram of reactions in the sintering process of ferronickel slag in the presence of magnesia

5.3.1.2 Phase Diagrams of the $MgO-SiO_2$ and $MgO-Fe_2O_3$ Systems

As shown in Fig. 5.4, forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$) are the two binary compounds in the $MgO-SiO_2$ system. The melting point of forsterite is 1890 °C and the eutectic temperature of forsterite and magnesia is 1850 °C. However, when forsterite and enstatite coexist, the eutectic temperature is very low, only 1557 °C. Therefore, in order to ensure that the refractory material prepared from the slag has high refractoriness, the formation of enstatite should be carefully controlled by adding enough magnesia.

For ferronickel slag sintered in oxidative atmosphere, olivine will undergo the reaction given by Eq. (5.27), forming forsterite, iron oxide, and silica. As mentioned above, the produced silica can react with magnesium oxide to form forsterite. As shown by Eq. (5.5), at 1200–1400 °C, iron oxide can react with magnesium oxide to produce magnesium ferrite spinel ($MgO \cdot Fe_2O_3$). The spinel is the only binary compound in the $MgO-Fe_2O_3$ system and its theoretical chemical composition is $w(MgO) = 20.1\%$ and $w(Fe_2O_3) = 79.9\%$. It is significantly dissolved in periclase (MgO) at 1000 °C or higher, producing magnesium stellite ($(Mg, Fe)O$). At nearly 1713 °C, the highest dissolved Fe_2O_3 content can reach 70%. Although the smelting point of magnesium ferrite spinel is 1713 °C, the smelting point of the formed solid solution can be increased when the spinel is dissolved in the periclase. It is obvious that the iron oxide from decomposition of olivine in the ferronickel slag can react with the magnesium oxide to form magnesium ferrite spinel with relatively high

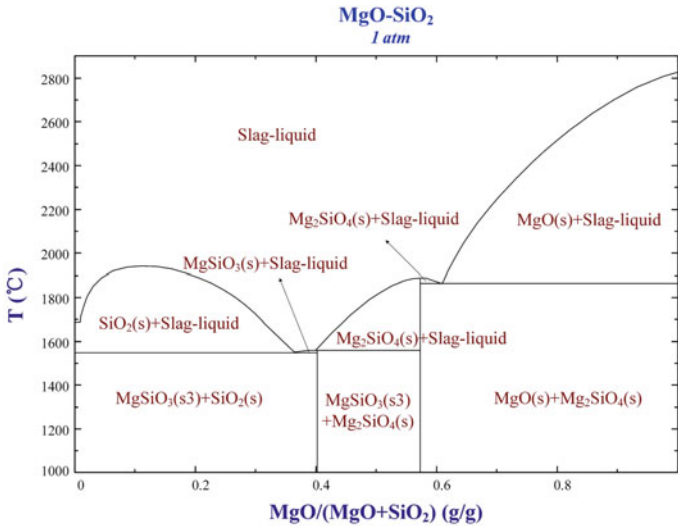
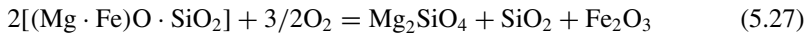


Fig. 5.4 Phase diagram of the MgO–SiO₂ system

melting point (1713 °C). Further, the spinel dissolved in the periclase can promote the sintering process (Fig. 5.5).



5.3.1.3 Phase Diagrams of the MgO–SiO₂–Fe₂O₃, MgO–SiO₂–Cr₂O₃, MgO–SiO₂–Al₂O₃, and MgO–SiO₂–CaO Systems

Except for MgO and SiO₂, Fe₂O₃, Cr₂O₃, Al₂O₃ and CaO are the main impurities in the ferronickel slag, the phase diagrams of the MgO–SiO₂–Fe₂O₃, MgO–SiO₂–Cr₂O₃, MgO–SiO₂–Al₂O₃ and MgO–SiO₂–CaO systems were calculated to explore the effects of Fe₂O₃, Cr₂O₃, Al₂O₃, and CaO on the refractoriness of the resulting refractory materials.

Figure 5.6 shows the phase diagram of the MgO–SiO₂–Fe₂O₃ system. The chemical compositions of triple invariable points and the corresponding eutectic temperatures are shown in Table 5.3. It can be observed from Fig. 5.6 that in the MgO–SiO₂–Fe₂O₃ system, with the change of the contents of magnesia, silica and iron oxide, the main phases formed include periclase (MgO), forsterite (Mg₂SiO₄), enstatite (MgSiO₃), cristobalite (SiO₂), tridymite (SiO₂), liquid, etc. As shown in Table 5.3, the melting temperature range of the eutectic phase formed by solid solution between different phases is from 1377 °C to 1465 °C. In comparison, the melting temperature of the eutectic phase formed by hematite in the system is lower. Among them, the melting temperature of the eutectic phase formed by hematite, enstatite, and

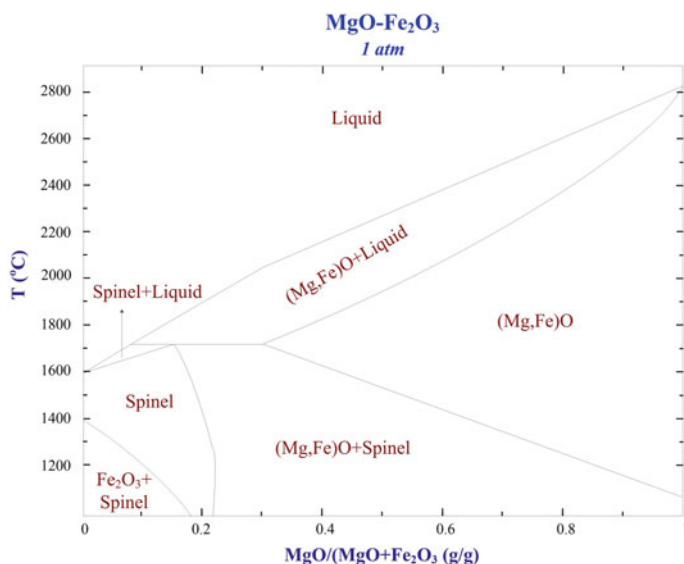


Fig. 5.5 Phase diagram of the MgO–Fe₂O₃ system

tridymite is the lowest, namely 1377 °C (point 5 in Fig. 5.6), which corresponds to 18.58 wt% magnesia, 51.86 wt% silica, and 29.56 wt% iron oxide, with the mass ratio of magnesia to silica of 0.36.

Figure 5.7 shows the phase diagram of the MgO–SiO₂–Cr₂O₃ system. The chemical compositions of triple invariant points and the corresponding eutectic points in the MgO–SiO₂–Cr₂O₃ system are shown in Table 5.4. According to Fig. 5.7, in the MgO–SiO₂–Cr₂O₃ system, the main phases include periclase, forsterite, spinel, enstatite, cristobalite, chromium oxide, liquid, etc. As shown in Table 5.4, the melting temperature range of the eutectic phase formed by solid solution between different phases is from 1534 °C to 1814 °C, showing a high eutectic temperature of the system. However, the presence of enstatite and cristobalite phases in the system will lower the melting temperature of the eutectic phase. Among them, the eutectic phase formed by periclase, forsterite, and spinel has the highest melting temperature of 1814 °C (point 1 in Fig. 5.7), which corresponds to the contents of 56.27 wt% magnesia, 35.14 wt% silica, and 8.59 wt% chromium oxide. The melting temperature of the eutectic phase formed by cristobalite, liquid, and spinel is 1723 °C (point 3 in Fig. 5.7) and the corresponding contents of magnesia, silica and chromium oxide are 22.52 wt%, 68.03 wt% and 9.45 wt%, respectively. The melting temperature of the eutectic phase formed by enstatite, cristobalite, and spinel is the lowest, namely 1534 °C (point 6 in Fig. 5.7), which corresponds to 34.56 wt% magnesia, 62.32 wt% silica, and 3.11 wt% chromium oxide.

Figure 5.8 shows the phase diagram of the MgO–SiO₂–Al₂O₃ system. The chemical compositions of triple invariant points and the corresponding eutectic points in the system are shown in Table 5.5. As shown in Fig. 5.8, the main phases in the

MgO–SiO₂–Al₂O₃ system include periclase, forsterite, enstatite, cordierite, sapphire, spinel, mullite, cristobalite and tridymite, etc. Table 5.5 shows that in the MgO–SiO₂–Al₂O₃ system the melting temperature range of the eutectic phase formed by solid solution between different phases varies from 1360 °C to 1646 °C. In the system, the melting temperature of the eutectic phase formed by spinel is relatively high. The melting temperature of the eutectic phase formed by periclase, forsterite and spinel is the highest, 1646 °C (point 1 in Fig. 5.8). At this moment, the corresponding contents of magnesia, silica, and alumina are 46.39 wt%, 38.41 wt%, and 15.20 wt%, respectively, and the corresponding mass ratio of magnesia to silica is 1.21.

Figure 5.9 shows the phase diagram of the MgO–SiO₂–CaO system. The component contents and eutectic temperatures of all ternary invariant points in the phase diagram are shown in Table 5.6. As shown in Fig. 5.9, in the MgO–SiO₂–CaO system, the main phases formed include periclase, forsterite, enstatite, limestone, merwinite, rankinite, wollastonite, diopside, cristobalite, tridymite, liquid, etc. Table 5.6 shows that in the MgO–SiO₂–CaO system there is a relatively large temperature range of the eutectic phase formed by solid solution between different phases, from 1327 °C to 1877 °C. The melting temperature of the eutectic phase formed by calcium silicate,

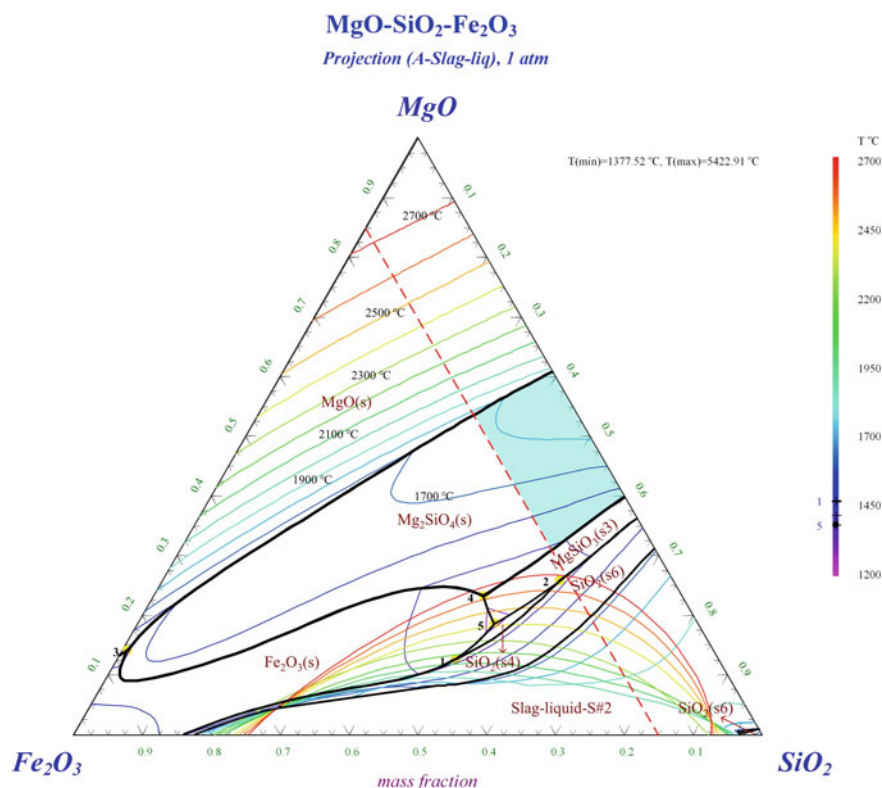


Fig. 5.6 Phase diagram of the MgO–SiO₂–Fe₂O₃ system

Table 5.3 Chemical compositions of triple invariable points and the corresponding eutectic points in the MgO–SiO₂–Fe₂O₃ system

No	Chemical composition (wt%)			Main phases	Eutectic point (°C)
	MgO	SiO ₂	Fe ₂ O ₃		
1	12.62	49.12	38.26	Hematite, cristobalite, and tridymite	1465
2	25.75	57.69	16.57	Enstatite, cristobalite, and tridymite	1465
3	14.01	0.75	85.24	Hematite, forsterite, and periclase	1461
4	23.28	47.87	28.85	Hematite, forsterite, and enstatite	1413
5	18.58	51.86	29.56	Hematite, enstatite, and tridymite	1377

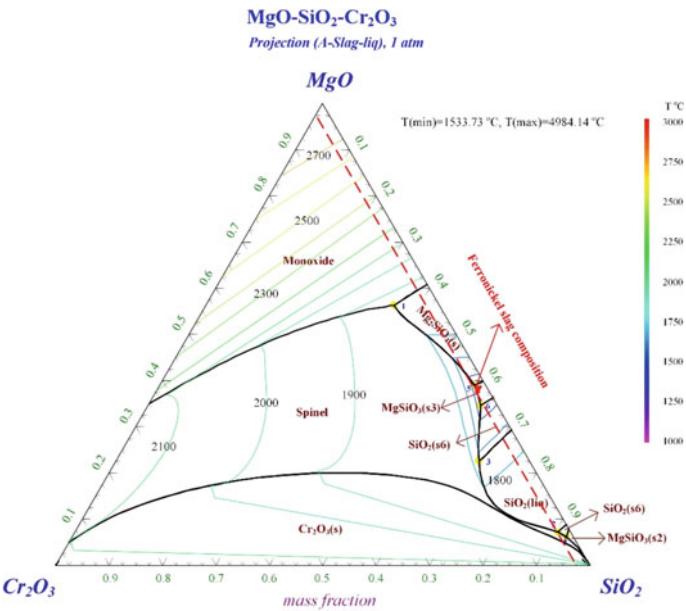


Fig. 5.7 Phase diagram of the MgO–SiO₂–Cr₂O₃ system

limestone, and periclase is as high as 1877 °C (point 1 in Fig. 5.9) and the corresponding contents of magnesia, silica and calcium oxide are 5.21 wt%, 31.04 wt% and 63.75 wt%, respectively. The melting temperature of the eutectic phase formed by calcium silicate, magnesite, and periclase can reach 1609 °C (point 2 in Fig. 5.9). The corresponding contents of magnesia, silicon dioxide and calcium oxide are 11.78 wt%, 36.70 wt% and 51.52 wt%, respectively. For obtaining high melting temperature of the eutectic phase in the system, the corresponding silica content

Table 5.4 Chemical compositions of triple invariable points and the corresponding eutectic points in the MgO–SiO₂–Cr₂O₃ system

No	Chemical composition (wt%)			Main phases	Eutectic point (°C)
	MgO	SiO ₂	Cr ₂ O ₃		
1	56.27	35.14	8.59	Forsterite, periclase, and spinel	1814
2	7.12	90.54	2.34	Cristobalite, liquid, and spinel	1723
3	22.52	68.03	9.45	Cristobalite, liquid, and spinel	1723
4	6.11	92.55	1.35	Enstatite, cristobalite, and spinel	1697
5	38.90	58.99	2.12	Enstatite, forsterite, and spinel	1547
6	34.56	62.32	3.11	Enstatite, cristobalite, and spinel	1534

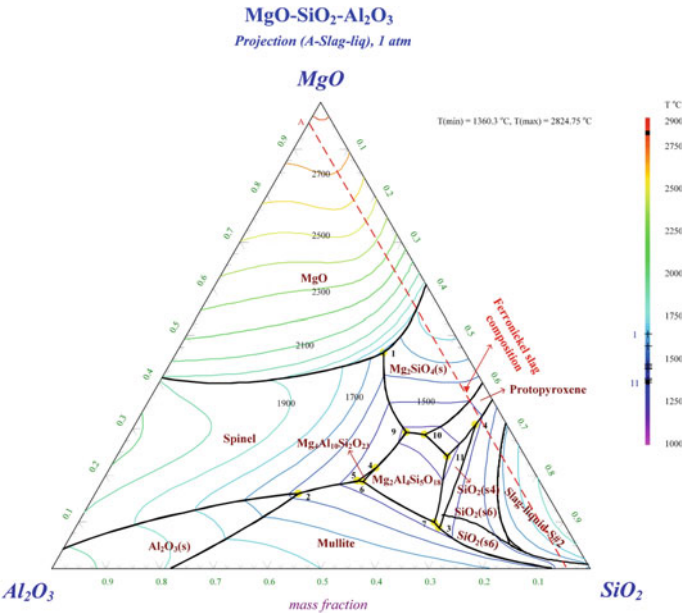


Fig. 5.8 Phase diagram of the MgO–SiO₂–Al₂O₃ system

is 31.04 wt%–36.70 wt% and the calcium oxide content is 51.52 wt%–63.75 wt%, which is unavailable in the actual ferronickel slag system. The melting temperature of the eutectic phase formed by forsterite is between 1351 °C and 1467 °C. Obviously, in the MgO–SiO₂–CaO system, forsterite easily forms eutectic compounds.

Table 5.5 Chemical compositions of triple invariable points and the corresponding eutectic points in the MgO–SiO₂–Al₂O₃ system

No	Chemical composition (wt%)			Main phases	Eutectic point (°C)
	MgO	SiO ₂	Al ₂ O ₃		
1	46.39	38.41	15.20	Periclase, forsterite, and spinel	1646
2	16.11	37.82	46.07	Spinel, corundum, and mullite	1575
3	8.66	67.67	23.67	Mullite, cristobalite, and tridymite	1465
4	30.82	63.28	5.90	Enstatite, cristobalite, and tridymite	1465
5	18.74	47.44	33.82	Spinel, sapphire, and mullite	1464
6	18.71	48.45	32.84	Cordierite, sapphire, and mullite	1455
7	9.89	66.10	24.01	Cordierite, mullite, and tridymite	1445
8	21.58	49.43	28.99	Spinel, cordierite, and sapphire	1440
9	29.25	19.53	51.22	Spinel, cordierite, and forsterite	1380
10	28.74	16.43	54.83	Enstatite, cordierite, and forsterite	1370
11	24.09	14.48	61.43	Enstatite, cordierite, and tridymite	1360

5.3.1.4 Phase Diagrams of the MgFe₂O₄–MgSi₂O₄, MgCr₂O₄–MgSi₂O₄, and MgAl₂O₄–MgSi₂O₄ Systems

In order to identify the effects of formed magnesium ferrite spinel, magnesium aluminate spinel, and magnesium chromate spinel on the refractoriness of refractory materials, the phase diagrams of the MgFe₂O₄–Mg₂SiO₄, MgCr₂O₄–Mg₂SiO₄, and MgAl₂O₄–Mg₂SiO₄ systems have been calculated. As shown in Fig. 5.10, the lowest liquid phase generation temperature of the MgFe₂O₄–Mg₂SiO₄ system is about 1720 °C. As shown in Fig. 5.11, the lowest liquid phase generation temperature of the MgCr₂O₄–Mg₂SiO₄ system is around 1800 °C. Obviously, the formation of spinel can improve the refractoriness of the refractory materials prepared from ferronickel slag. As shown in Fig. 5.12, the lowest liquid phase generation temperature of the MgAl₂O₄–Mg₂SiO₄ system is approximately 1650 °C. It indicates that the formation of magnesium aluminate spinel should be carefully controlled.

Based on the above thermodynamic analysis, it can be concluded that by sintering ferronickel slag with the addition of magnesia at appropriate temperatures, it is possible to promote the formation of forsterite and spinel phases (magnesium ferrite

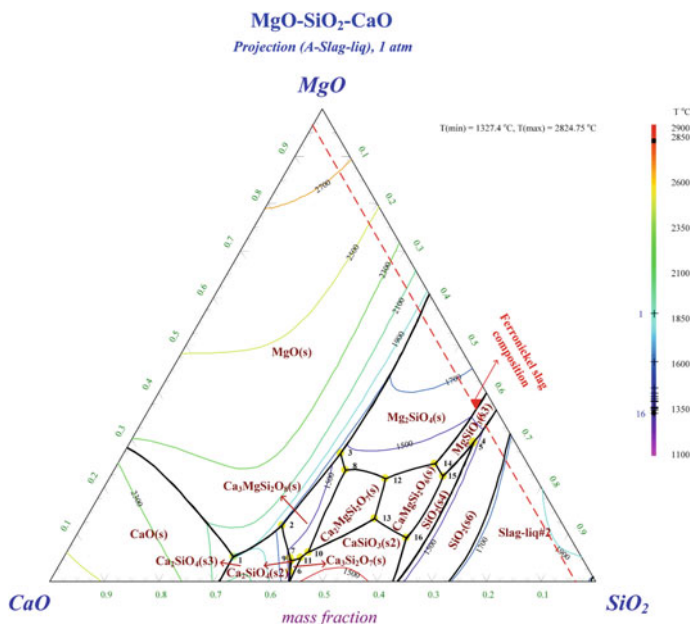


Fig. 5.9 Phase diagram of the MgO-SiO₂-CaO system

spinel, magnesium aluminate spinel, and magnesium chromate spinel), which would improve refractoriness of the refractory materials derived from the slag.

5.3.2 Technology for Preparing Refractory Materials from Ferronickel Slag

Based on the above theoretical analysis, the feasibility of a new and efficient technological route for preparing forsterite refractory materials from ferronickel slag was verified by altering its chemical and phase compositions in the presence of low-cost sintered magnesia. In addition, the effects of sintering temperature, sintering time, and content of chromium oxide on the properties of refractory materials were evaluated.

The ferronickel slag sample was obtained from the RKEF process of a ferronickel smelting plant in China. Its chemical composition is shown in Table 5.7. The sample was characterized by very low content of nickel oxide (0.06 wt%), high contents of silica and magnesia (48.29 and 30.95 wt%, respectively), and low magnesia to silica ratio (0.64). The X-ray diffraction (XRD) pattern (Fig. 5.13) shows that the slag was mainly composed of olivine. The SEM-EDS analysis of ferronickel slag (Fig. 5.14) shows that its microstructure was constituted by three different colored regions. The dark region (point 1 in Fig. 5.14) contained a phase whose chemical composition

Table 5.6 Chemical compositions of triple invariable points and the corresponding eutectic points in the MgO–SiO₂–CaO system

No	Chemical composition (wt%)			Main phases	Eutectic point (°C)
	MgO	SiO ₂	CaO		
1	5.21	31.04	63.75	Calcium silicate, limestone, and periclase	1877
2	11.78	36.70	51.52	Calcium silicate, magnesite, and periclase	1609
3	27.04	39.81	33.15	Forsterite, forsterite, and periclase	1467
4	29.51	62.99	7.50	Enstatite, cristobalite, and tridymite	1465
5	29.19	63.03	7.78	Enstatite, cristobalite, and tridymite	1465
6	2.07	43.01	54.91	Calcium silicate, calcium silicate, and wollastonite	1437
7	4.90	41.58	53.52	Calcium silicate, calcium silicate, and magnesite	1437
8	23.53	42.41	34.06	Magnesite, magnesia, and forsterite	1418
9	4.25	42.14	53.61	Calcium silicate, magnesia wollastonite, and wollite	1406
10	6.14	44.28	49.58	Magnesite, magnesite, and wollastonite	1392
11	4.92	43.51	51.57	Wollastonite, wollastonite, and wollastonite	1389
12	21.76	50.66	27.58	Forsterite, diopside, and forsterite	1358
13	13.20	52.87	33.93	Wollastonite, diopside, and wollastonite	1357
14	24.86	58.17	16.97	Diopside, forsterite, and enstatite	1351
15	22.26	60.93	16.81	Diopside, enstatite, and tridymite	1341
16	9.13	60.78	30.09	Diopside, wollastonite, and tridymite	1327

was close to olivine, which agreed with the XRD results. The gray region (point 2 in Fig. 5.14) had a complex chemical composition with silica as the main ingredient. Between the gray and dark regions, a darker gray region (point 3 in Fig. 5.14), with the chemical composition close to that of the gray region, was observed. Sintered magnesia was used as a source of MgO in this study due to its relatively high MgO content, low cost (\$200–300/t), and high availability. The chemical composition of sintered magnesia is given in Table 5.8, which shows the content of MgO was 94.51 wt%. The XRD pattern (Fig. 5.15) shows that the sintered magnesia mainly consisted of periclase. Magnesium chloride of analytical grade was used as a binder in the preparation of refractory materials from ferronickel slag.

Initially, the grounded ferronickel slag (86 wt% of the particles passing 74 μm sieve) and sintered magnesia (89 wt% of the particles passing 74 μm sieve) were carefully mixed in a planetary ball mill for 20 min. The briquettes of 20 mm in diameter and 20 mm in height were produced by manual hydraulic pressing at 100 MPa using 5 wt% magnesium chloride solution (1.3 g/cm³) as the binder. They were then dried in a vacuum drying oven at 105 °C for 4 h. After drying, the briquettes were

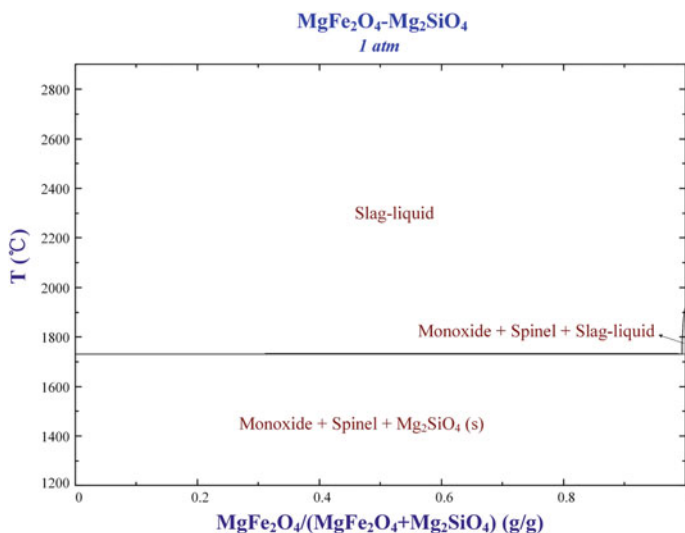


Fig. 5.10 Phase diagram of the $\text{MgFe}_2\text{O}_4\text{-MgSi}_2\text{O}_4$ system

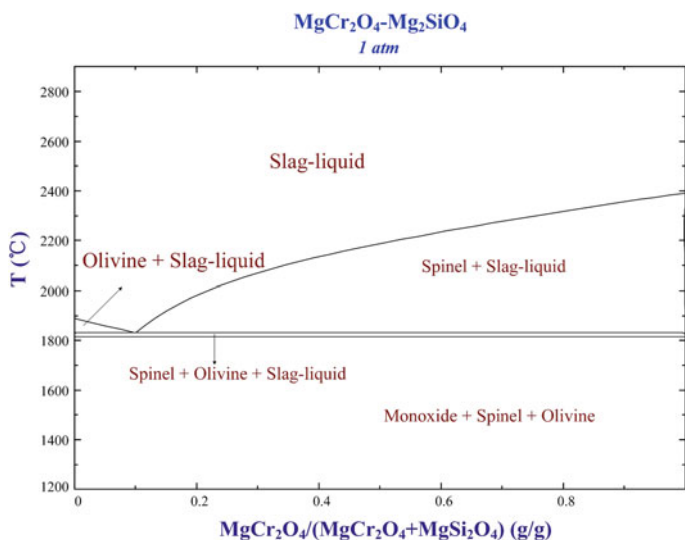


Fig. 5.11 Phase diagram of the $\text{MgCr}_2\text{O}_4\text{-MgSi}_2\text{O}_4$ system

placed in a muffle furnace before sintering at a designated temperature for a given time period. Then, the briquettes were cooled to room temperature and then taken out for the subsequent characterization tests.

The chemical compositions of the samples were examined using an X-ray fluorescence spectrometer (XRF, PANalytical, Axios mAX, Almelo, The Netherlands). The

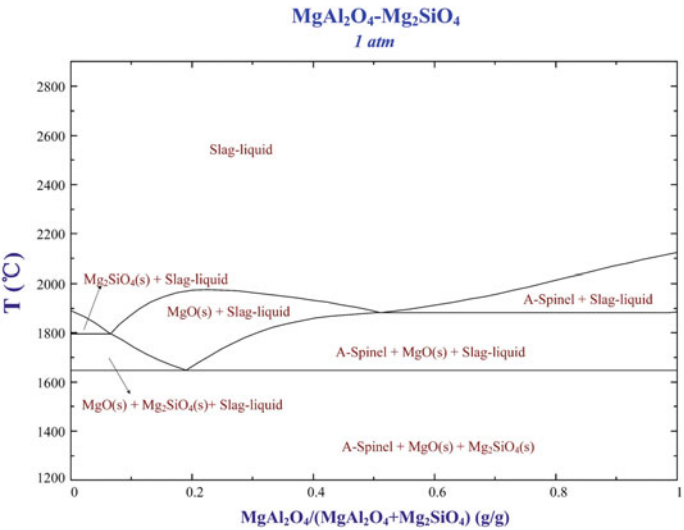


Fig. 5.12 Phase diagram of the MgAl₂O₄-MgSi₂O₄ system

Table 5.7 Main chemical composition of ferronickel slag

Component	FeO	NiO	SiO ₂	CaO	MgO	Al ₂ O ₃	Cr ₂ O ₃
Content (wt%)	7.39	0.06	48.29	2.40	30.95	4.04	2.11

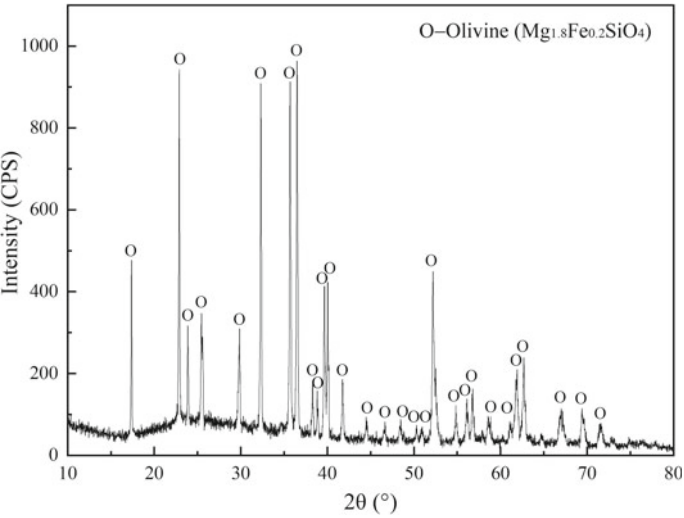


Fig. 5.13 XRD pattern of ferronickel slag

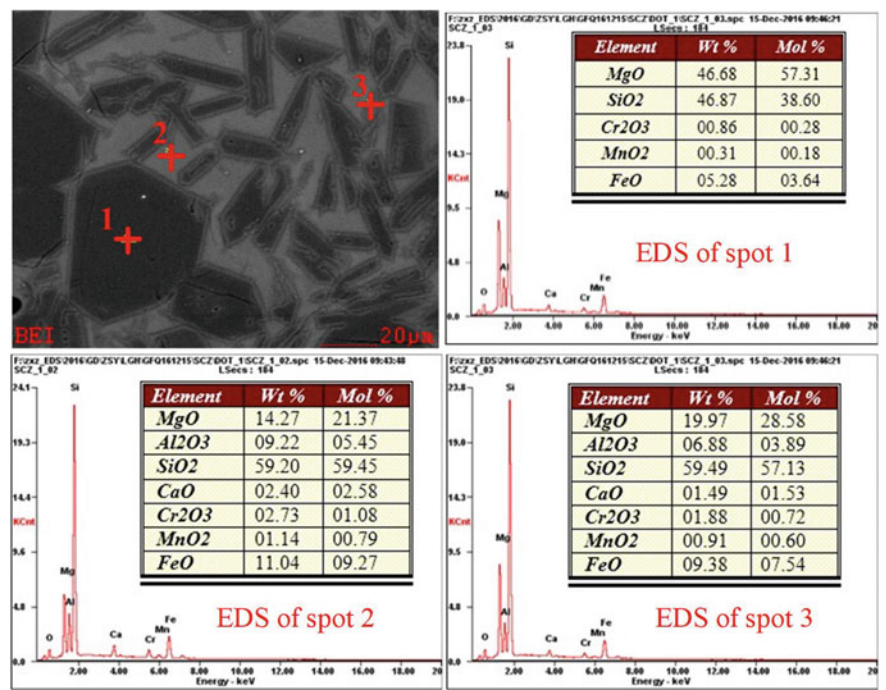


Fig. 5.14 SEM–EDS analysis of ferronickel slag, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

Table 5.8 Main chemical composition of sintered magnesia

Component	MgO	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
Content (wt%)	94.51	1.53	0.98	1.13	0.65

phase constituents of the samples were identified by an X-ray diffraction spectrometer (XRD, D/max 2550PC, Japan Rigaku Co., Ltd.) using a Cu-anode target with the wavelength of 1.54056 Å, scan mode for the step scan, and step length of 0.02°. The morphological change of the sample during sintering was detected by using an electron scanning electron microscope (ESEM; FEI QUANTA 200; FEI, Eindhoven, The Netherlands) equipped with an EDAX energy dispersive X-ray spectroscopy (EDS) detector (EDAX Inc., Mahwah, NJ).

The values of refractoriness, bulk density and apparent porosity, and compressive strength of the refractory materials were measured according to the Chinese National Standard Test Methods (GB/T 7322–2007, GB/T 2997–2000, and GB/T 5072–2008, respectively).

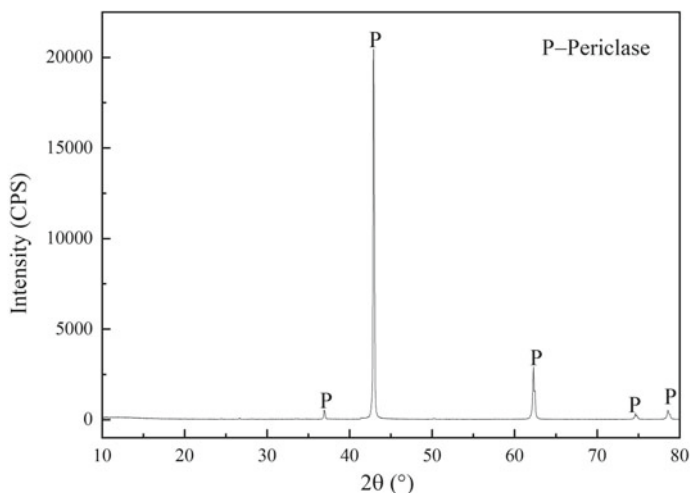


Fig. 5.15 XRD pattern of sintered magnesia

5.3.2.1 Effect of Magnesia Addition

The phase transformation of ferronickel slag in the presence of magnesia during the sintering process was experimentally determined by investigating the effect of addition of magnesia varying from 0 to 35 wt% at the sintering temperature of 1350 °C for 3 h. The obtained refractory materials were characterized by the XRD and SEM-EDS techniques.

Figure 5.16 shows the XRD patterns of the refractory materials obtained by sintering with different additions of magnesia. The main phases of the refractory materials prepared by sintering without the addition of magnesia were olivine and enstatite, which were close to those of the slag. When the addition of magnesia increased to 5 wt%, forsterite and magnesium chromate spinel were observed. By further increasing the addition of magnesia, forsterite and magnesium chromate spinel remained, while enstatite gradually disappeared. When the addition of magnesia was higher than 15 wt%, the magnesium aluminate spinel formed. As the addition of magnesia increased continuously to 25 wt%, there was a periclase phase. These phase conversions are summarized in Fig. 5.17. Obviously, the original phase, olivine, in the slag underwent four consecutive stages of phase transformation during the sintering process with increasing amount of magnesia. The addition of magnesia could facilitate generation of high-refractoriness phases.

The morphologies of the refractory materials sintered were examined by the SEM-EDS technique. The results of sample 1 (addition of 0 wt% magnesia, 1350 °C, 3 h), sample 2 (addition of 20 wt% magnesia, 1350 °C, 3 h), sample 3 (addition of 35 wt% magnesia, 1350 °C, 3 h) and sample 4 (addition of 20 wt% magnesia, 1350 °C, 5 h) are shown in Figs. 5.18, 5.19, 5.20 and 5.21, respectively. As shown in Fig. 5.18, the morphologies of sample 1 had obviously changes compared with those of ferronickel

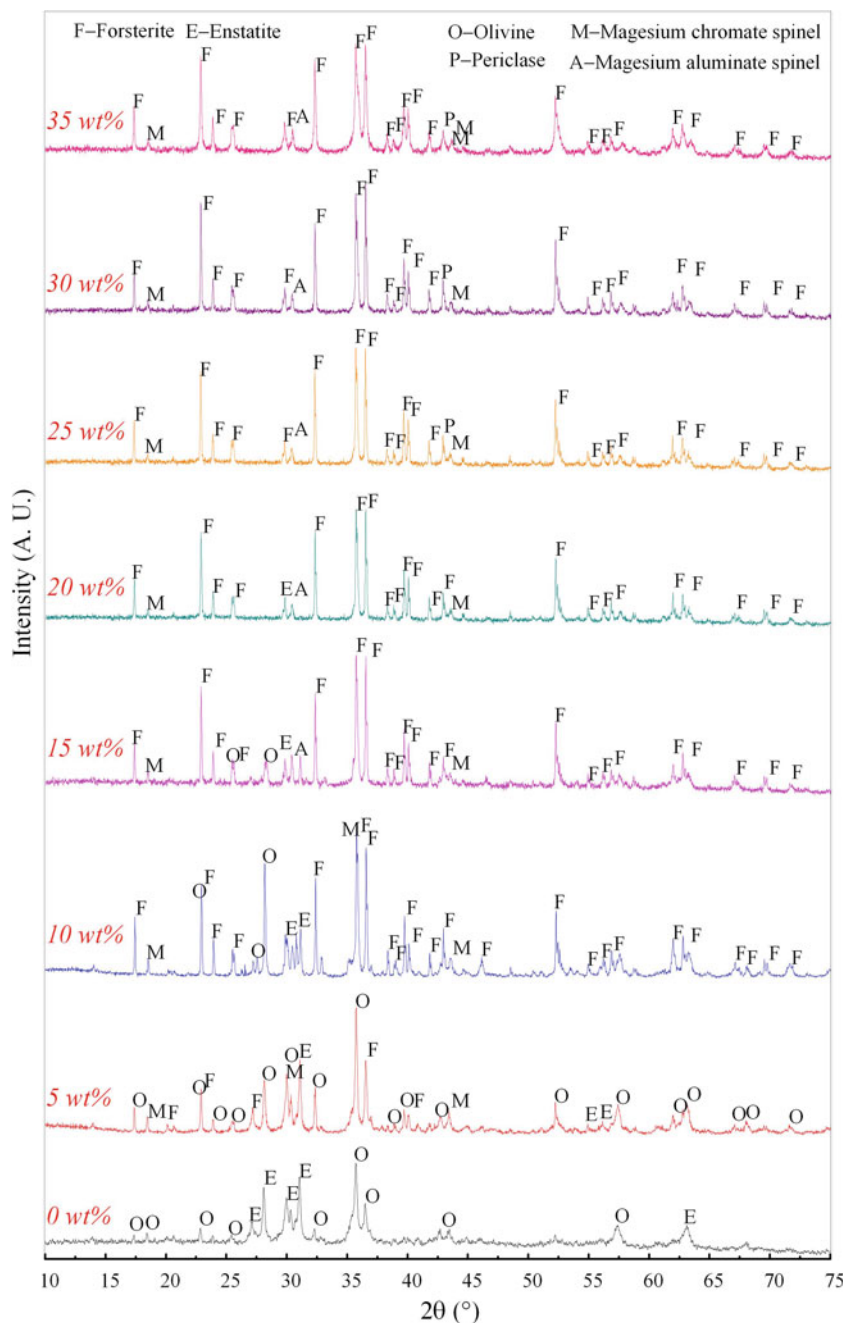


Fig. 5.16 XRD patterns of the refractory materials obtained by sintering with different additions of magnesia, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

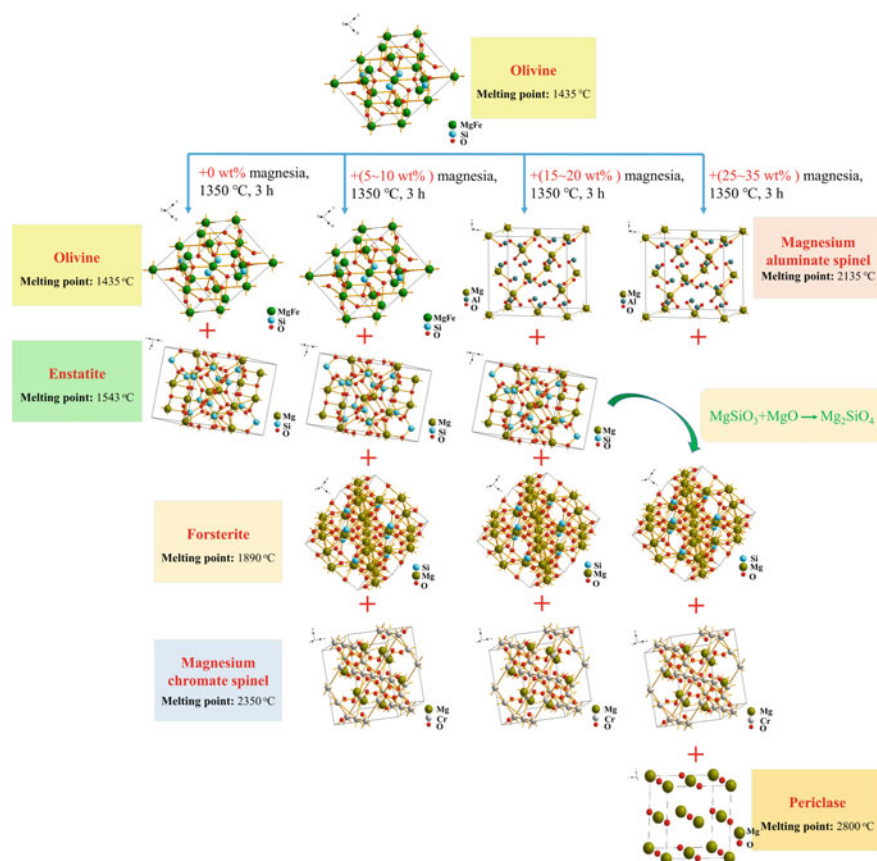


Fig. 5.17 Phase transformation of the refractory materials obtained by sintering with different magnesia additions, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

slag. The sample 1 presented three different phases. As revealed by EDS results in Fig. 5.18, spots 1–3 were constituted by an iron-rich phase, a silica-rich phase and olivine, respectively. As shown in Figs. 5.19 and 5.20, with increasing magnesia addition, the phases had slight changes. The iron contents in the iron-rich phase and olivine phase were gradually decreased, while the content of the magnesium in these three phases was increased. Based on the XRD results in Fig. 5.16, it was inferred that the olivine in ferronickel slag would undergo decomposition, producing a low-iron olivine phase and enstatite. During the sintering process, the enstatite reacted with the sintered magnesia, forming forsterite. The components of iron, aluminum and chromium were enriched in the phase of spot 1, producing spinel. Compared with spots 1 and 3, spot 2 was composed of a low-magnesium transient phase, which would eventually change to the spinel phases. With increasing sintering time and magnesia addition, the amount of the transient phase decreased considerably.

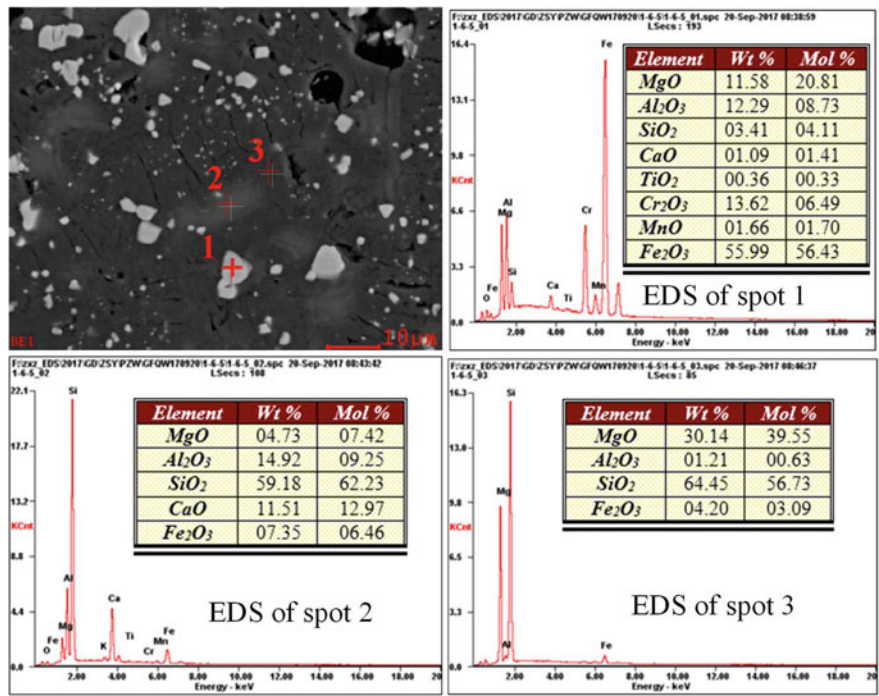


Fig. 5.18 SEM–EDS analysis of the refractory material obtained by sintering at 1350 °C for 3 h with the addition of 0 wt% magnesia, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

The effect of magnesia addition on the refractoriness of the refractory material was studied when the sample was sintered at 1350 °C for 3 h. As shown in Fig. 5.22, when the magnesia addition increased from 0 to 20 wt%, the refractoriness of the refractory material increased from 1438 to 1660 °C. With further increase of the magnesia addition, the refractoriness of the refractory material increased slightly. According to the changing trend of refractoriness, one can divide it into three stages with increasing addition of magnesia. As shown in Fig. 5.22, within the addition range of 0–10 wt% magnesia, olivine remained as the dominant phase, producing a refractory material with low refractoriness. In the addition range of 10–20 wt% magnesia, the amounts of forsterite and spinel increased continuously, significantly enhancing the refractoriness of the refractory material. When the addition of magnesia increased to 20–35 wt%, the forsterite and spinel phases became dominant, leading to a high refractoriness. These results demonstrated that adding magnesia facilitated the formation of high melting point phases, thereby substantially promoting refractory property of the target material.

The effects of magnesia addition on the bulk density, apparent porosity, and compressive strength of refractory material were also evaluated under the same sintering conditions, as shown in Fig. 5.23. When the magnesia addition increased

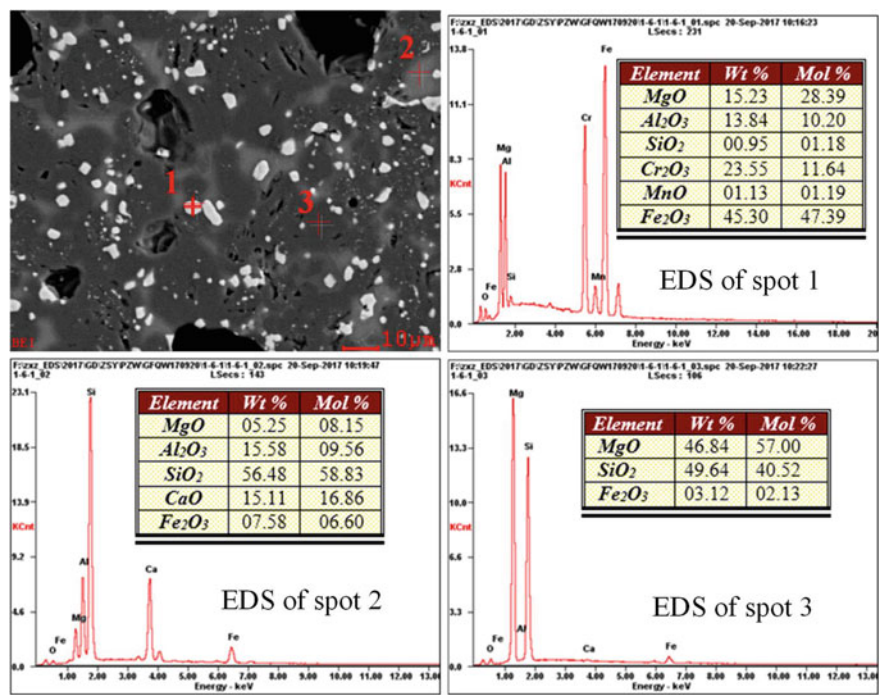


Fig. 5.19 SEM–EDS analysis of the refractory material obtained by sintering at 1350 °C for 3 h with the addition of 20 wt% magnesia, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

from 0 to 5 wt%, the bulk density of the refractory material decreased from 2.85 to 2.74 g/cm³. As the magnesia addition was further increased, the bulk density of the refractory material increased gradually. With the addition of 20 wt% magnesia, the bulk density reached the maximum value. However, as the magnesia addition exceeded 20 wt%, the bulk density of the refractory material decreased significantly. Obviously, the changes were closely associated with the phase transformation of the sample during sintering. There was massive liquid phase (olivine) formed in the refractory material in the absence of magnesia, contributing to the densification of the material. This was followed by a reduction in densification caused by a little addition of magnesia (up to 5 wt%). However, with increasing magnesia addition to 20 wt%, the phase transformation of the refractory material became more complete, promoting densification of the material with higher bulk density. Meanwhile, the negative effect of liquid phase on the refractoriness was restrained. When the magnesia addition increased continuously, the amount of spinel increased. Because the recrystallization capacity of spinel is weak and its formation is accompanied by a large volume expansion, which is harmful to the densification of the material, excessive magnesia addition will lower the bulk density of the refractory material. As expected, the changing tendency of bulk density was opposite to the

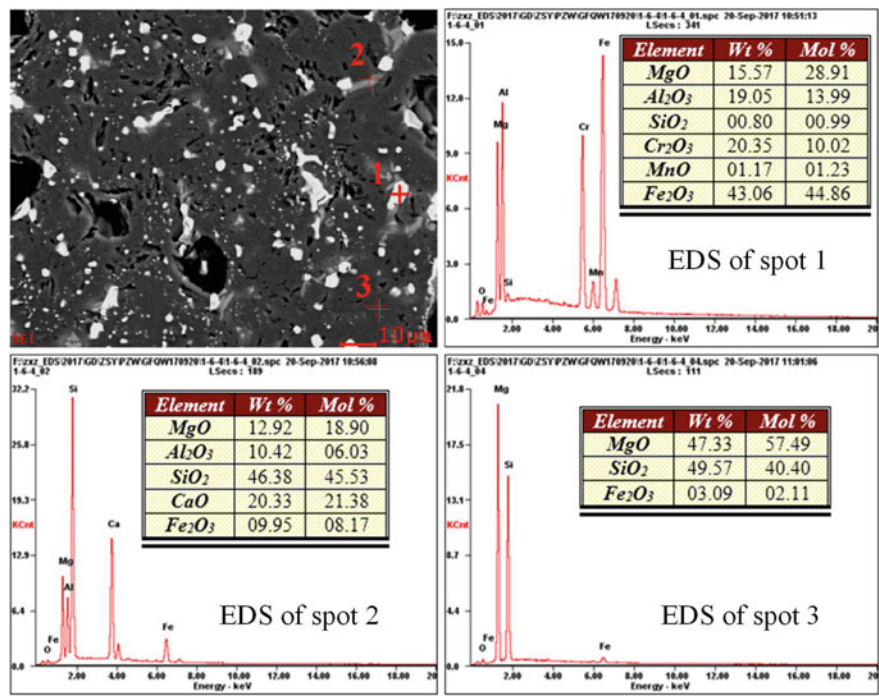


Fig. 5.20 SEM–EDS analysis of the refractory material obtained by sintering at 1350 °C for 3 h with the addition of 35 wt% magnesia, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

variation of apparent porosity but was consistent with that of compressive strength of the refractory material.

The effect of magnesia addition on the hydration resistance of the refractory material was evaluated under the same sintering conditions, as shown in Table 5.9. As the addition of magnesia increased, the mass increase percentage of the refractory material after hydration experiments increased. Overall, the mass increase percentage of the refractory material remained at a very low level, indicated that the refractory material had great hydration resistance.

The water quenching method was used to test the thermal shock resistance of refractory material. At first, the refractory material samples were placed in a 1100 °C muffle furnace for 20 min. Then, the samples were cooled in a water tank for 3 min, and dried in air for 5 min. After drying, the samples were taken back to the muffle furnace. This operation was repeated until the sample surface cracked and the cycle number was recorded. The test results are shown in Table 5.10. As the addition of magnesia exceeded 20 wt%, the thermal shock resistance of the sample began to deteriorate.

The main chemical components of the samples obtained with different magnesia additions are shown in Table 5.11. When the magnesia addition was 20 wt%, the

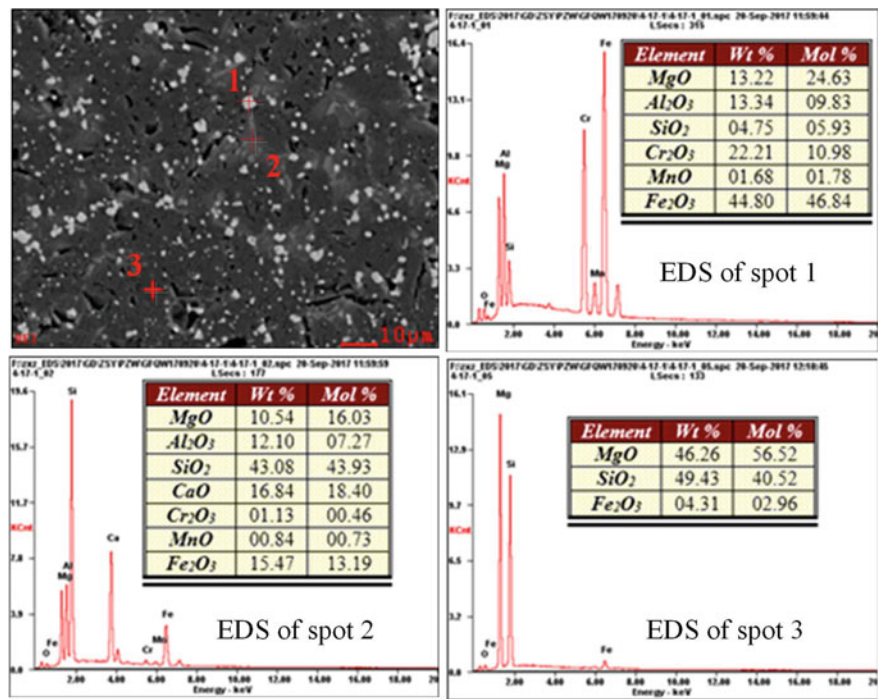


Fig. 5.21 SEM–EDS analysis of the refractory material obtained by sintering at 1350 °C for 5 h with the addition of 20 wt% magnesia, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

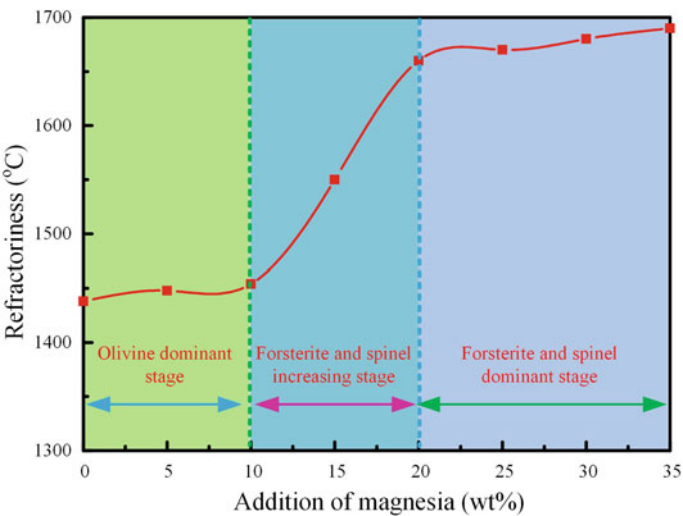


Fig. 5.22 Effect of magnesia addition on the refractoriness of the refractory material, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

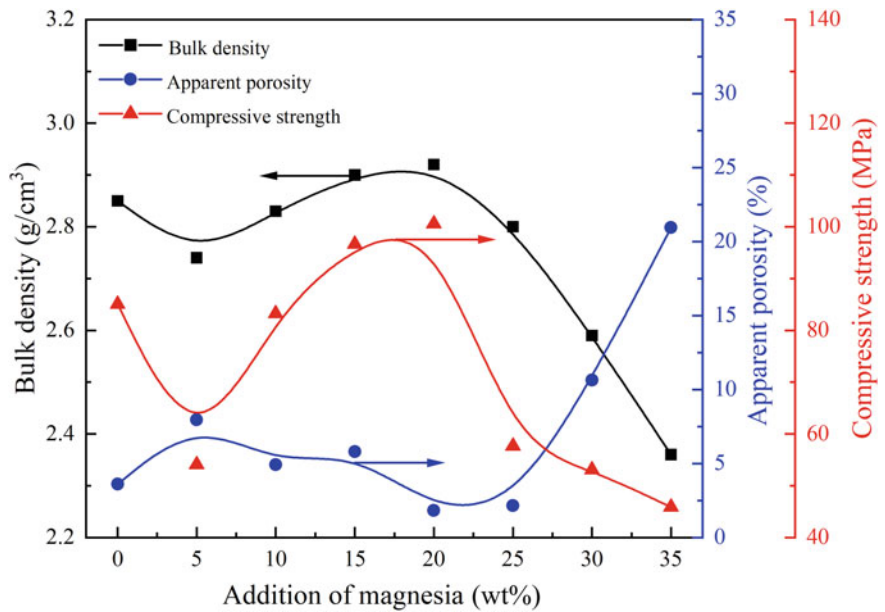


Fig. 5.23 Effects of magnesia addition on the bulk density, apparent porosity, and compressive strength of refractory material, reprinted from Ref. [24], copyright 2018, with permission from the American Chemical Society

Table 5.9 Effect of magnesia addition on the mass increase percentage of the refractory material after hydration experiments

Addition of magnesia (wt%)	5	10	15	20	25	30	35
Mass increase percentage (wt%)	0.009	0.007	0.002	0.004	0.007	0.011	0.027

Table 5.10 Effect of addition of magnesia on the thermal shock resistance of the refractory material

Addition of magnesia (wt%)	5	10	15	20	25	30	35
Cycle	2	2	4	4	2	2	2

MgO/SiO₂ mass ratio was 1.38, which was the closest to the MgO/SiO₂ mass ratio of forsterite.

5.3.2.2 Effect of Sintering Temperature

The effect of sintering temperature (1200–1500 °C) on the phase composition and microstructure of the slag in the presence of 20 wt% sintered magnesia for preparation of refractory materials was determined based on the XRD and SEM–EDS analyses.

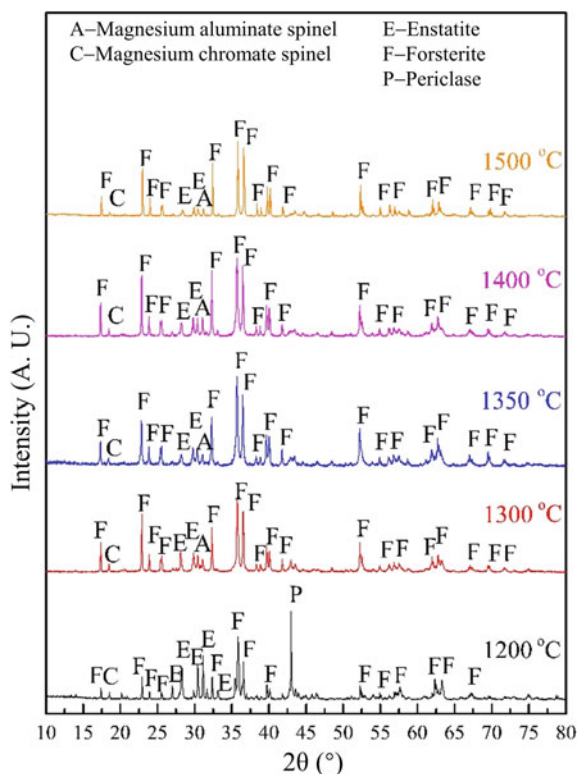
Table 5.11 Main chemical components of the refractory materials obtained with different magnesia additions

Addition of magnesia (wt%)	Main chemical components (wt%)					(MgO/SiO ₂)
	MgO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	
5	37.84	38.74	9.50	3.98	1.23	0.98
10	40.44	36.32	9.06	3.72	1.22	1.11
15	42.49	35.85	9.26	3.62	1.22	1.19
20	45.54	33.05	8.91	3.76	1.21	1.38
25	49.28	32.86	8.79	3.42	1.28	1.50
30	51.06	31.69	8.45	3.26	1.31	1.61
35	53.03	30.39	7.79	3.40	1.30	1.74

Figure 5.24 shows the XRD patterns of the refractory materials obtained by sintering at different temperatures for 3 h. The primary phases of the material obtained at 1200 °C were forsterite, enstatite, periclase and magnesium chromate spinel. When the sintering temperature increased to 1300 °C, the diffraction peaks of magnesium aluminate spinel appeared, whereas those assigned to periclase disappeared. Meanwhile, the intensity of diffraction peaks of enstatite decreased significantly. The sintered magnesia had incomplete reaction with ferronickel slag at temperatures below 1300 °C. As the sintering temperature was further increased to 1400 °C, the main phases of the refractory materials became forsterite, magnesium chromate spinel, magnesium aluminate spinel and enstatite. When the temperature grew continuously to 1500 °C, however, no apparent changes were observed, which agreed well with the thermodynamic analysis. Note that independent iron-containing phases were not observed due to the migration of iron oxide generated from decomposition of olivine, which was verified by the SEM–EDS analysis (Figs. 5.25 and 5.26). In the sintering process, forsterite and spinel became more dominant with decrease of enstatite. This change favored the enhancement of refractoriness of the refractory material because the existence of enstatite would cause a low eutectic temperature (1557 °C) with forsterite which had a negative impact on the property of the prepared material.

The SEM–EDS analyses of the obtained refractory materials were carried out. Figures 5.25, 5.26 and 5.27 show the results of sample 1 (20 wt% sintered magnesia, 1200 °C, 3 h), sample 2 (20 wt% sintered magnesia, 1400 °C, 3 h), and sample 3 (20 wt% sintered magnesia, 1500 °C, 3 h), respectively. For sample 1, the spots 1–3 in Fig. 5.25 were constituted by forsterite, enstatite, and spinel, respectively. The spot 4 was composed of periclase, resulting from the incompleteness of reaction between sintered magnesia and the slag at 1200 °C. As shown in Fig. 5.26, the sample 2 presented three main phases at the sintering temperature of 1400 °C, including forsterite (spot 1), spinel (spot 2), and a silica-rich phase (a glassy phase, spot 3) which would facilitate the densification of the refractory material. At this moment, periclase disappeared, in agreement with the XRD results. As shown in Fig. 5.27, with further increase of the sintering temperature to 1500 °C, the phases of sample 3

Fig. 5.24 XRD patterns of the refractory materials obtained by sintering at different temperatures, reprinted from Ref. [25], copyright 2019, with permission from the Minerals, Metals and Materials Society



changed slightly. It was also found that the grain size of spinel increased significantly with sintering temperature, from about 0.5 μm at 1200 °C to 2.5 μm at 1400 °C, and then to 5 μm at 1500 °C. This phenomenon was probably attributed to the increased content of liquid phase at higher temperatures which could promote the growth of spinel particles because of accelerated mass transfer. In fact, according to the theoretically calculation by FactSage 7.2, the content of liquid phase increased from 0% to 27.34% when the temperature increased from 1200 °C to 1500 °C. Hence, higher sintering temperature is expected to promote the generation of high-refractoriness phases, including forsterite and spinel phases. However, the rapid growth of spinel phases caused by elevating temperature may restrain the densification of the prepared material because the formation of spinel during the sintering process is usually accompanied by a large volume expansion due to its weak recrystallization capacity.

The effect of sintering temperature on the refractoriness of the refractory material was investigated when the slag was sintered with the addition of 20 wt% sintered magnesia at different temperatures for 3 h. As shown in Fig. 5.28, in the temperature range from 1200 °C to 1400 °C, the refractoriness of the refractory material increased obviously from 1580 °C to 1680 °C. However, when the sintering temperature was further increased to 1500 °C, the refractoriness of the refractory material increased

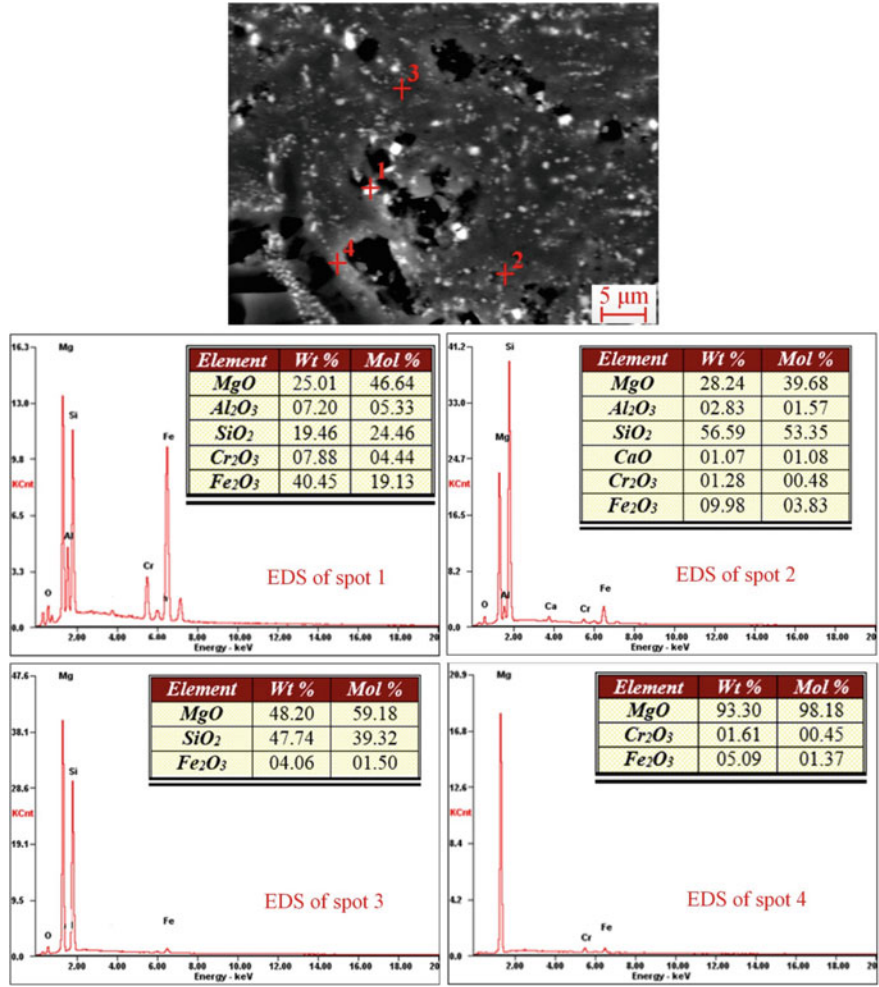


Fig. 5.25 SEM–EDS analysis of the refractory material obtained by sintering at 1200 °C, reprinted from Ref. [25], copyright 2019, with permission from the Minerals, Metals and Materials Society

slightly. According to the above analysis, this initial rapid increase in refractoriness was attributed to the increased generation of forsterite and spinel phases as well as lower enstatite content. When the sintering temperature exceeded 1400 °C, the main phases of the refractory material remained relatively constant, apart from the increased size of spinel grains (white spots in the insets of Fig. 5.28). Hence, there was a smaller increment of the refractoriness of the refractory material.

The effects of sintering temperature on the bulk density, apparent porosity and compressive strength of the refractory material were also studied, as shown in Fig. 5.29. When the sintering temperature increased from 1200 °C to 1400 °C, the bulk density of the refractory material increased from 2.41 g/cm³ to 2.93 g/cm³

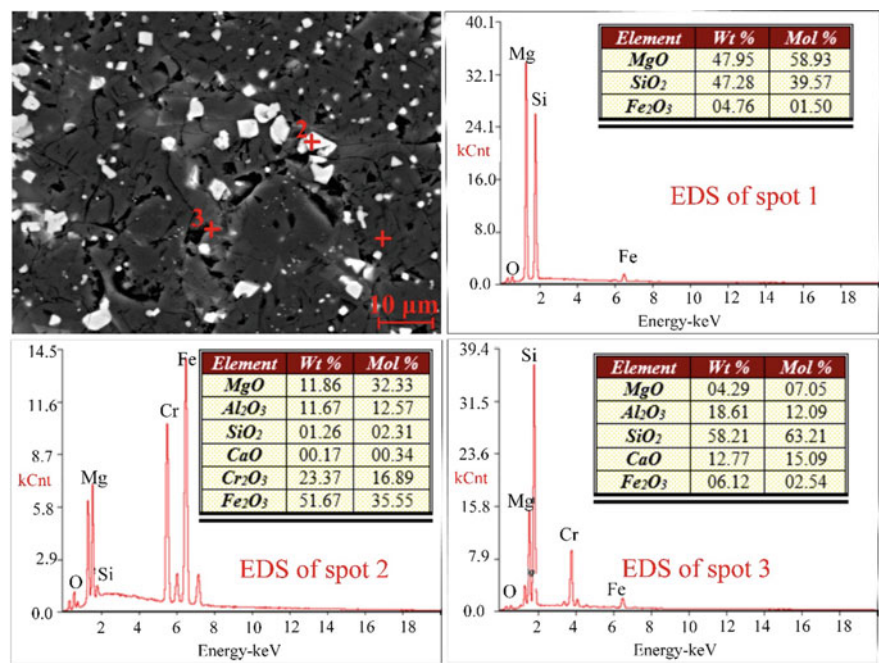


Fig. 5.26 SEM–EDS analysis of the refractory material obtained by sintering at 1400 °C, reprinted from Ref. [25], copyright 2019, with permission from the Minerals, Metals and Materials Society

and the compressive strength of the refractory material grew from 67.32 MPa to 166.62 MPa. As the sintering temperature increased continuously, the bulk density and compressive strength of the refractory material declined. The changing tendency of apparent porosity was opposite to the variations of the bulk density and compressive strength of the refractory material. Without doubt, these changes could be attributed to the phase and microstructure transformations of the material during the sintering process. At lower temperatures (1200–1400 °C), the increase of liquid phase in the system would contribute to the densification of the sample which counteracted the large volume expansion accompanied by the spinel formation. As the sintering temperature increased from 1400 °C to 1500 °C, the grain size of spinel grew from 2.5 µm to 5 µm rapidly. Because of the fast growth of spinel with a potential unfavorable impact on the densification of the material, the bulk density and compressive strength decreased while the apparent porosity increased.

The effect of sintering temperature on the hydration resistance of the refractory material was evaluated under the same sintering conditions, as shown in Table 5.12. As the sintering temperature increased, the mass increase percentage of the refractory material after hydration experiments changed minorly. When the sintering temperature was 1350 °C, the mass increase percentage of the refractory material was only 0.004 wt%, showing its great hydration resistance.

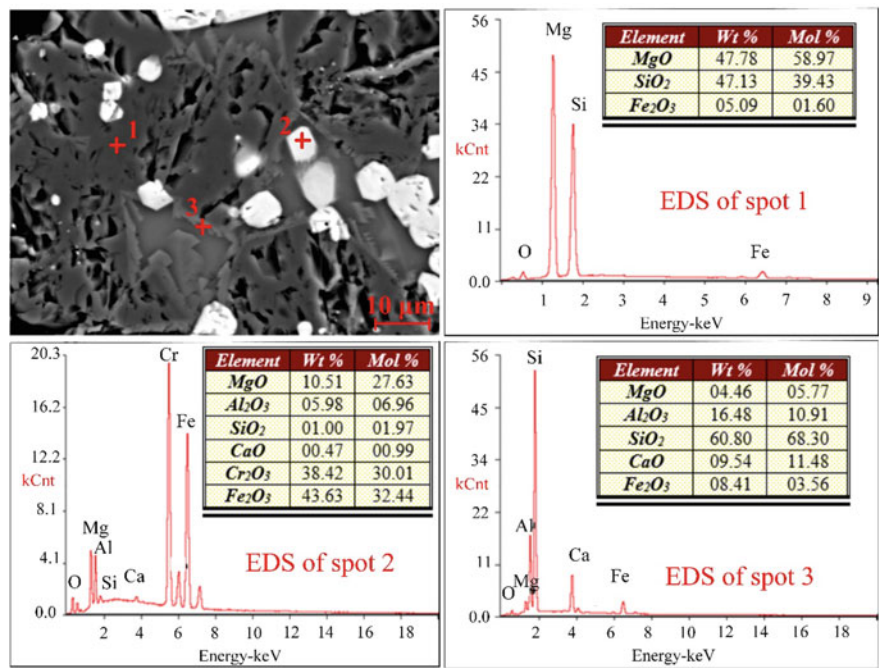


Fig. 5.27 SEM–EDS analysis of the refractory material obtained by sintering at 1500 °C, reprinted from Ref. [25], copyright 2019, with permission from the Minerals, Metals and Materials Society

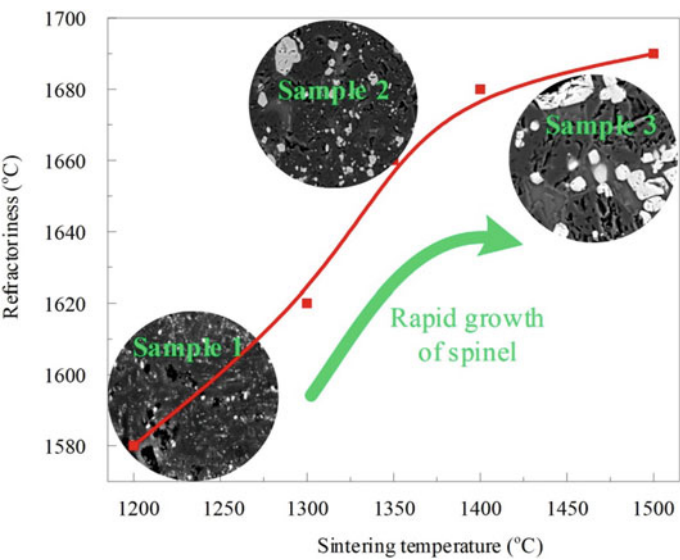


Fig. 5.28 Effect of sintering temperature on the refractoriness of the refractory material, reprinted from Ref. [25], copyright 2019, with permission from the Minerals, Metals and Materials Society

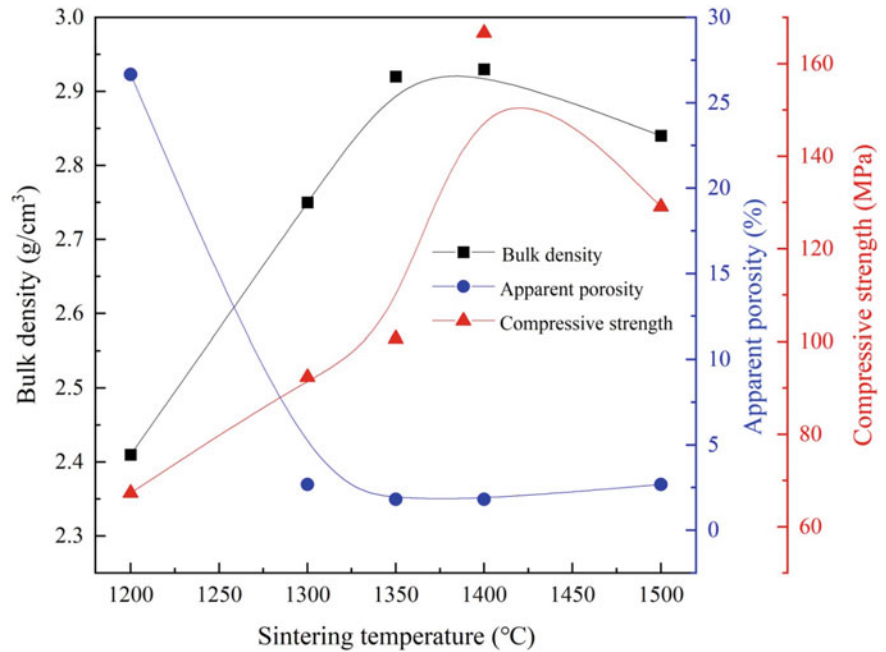


Fig. 5.29 Effect of sintering temperature on the bulk density, apparent porosity, and compressive strength of the refractory material, reprinted from Ref. [25], copyright 2019, with permission from the Minerals, Metals and Materials Society

Table 5.12 Effect of sintering temperature on the mass increase percentage of the refractory material after hydration experiments

Sintering temperature (°C)	1250	1300	1350	1400	1450	1500
Mass increase percentage (wt%)	0.035	0.005	0.004	0.005	0.022	0.025

The thermal shock resistance test results of the refractory material are shown in Table 5.13. When the sintering temperature was 1350 °C, the thermal shock resistance of the refractory material was 4 cycles. As the sintering temperature further increased, the resistance declined.

Table 5.13 Effect of sintering temperature on the thermal shock resistance of the refractory material

Sintering temperature (°C)	1250	1300	1350	1400	1450	1500
Cycle	2	1	4	3	1	1

5.3.2.3 Effect of Sintering Time

The effect of sintering time (1–5 h) on the phase and microstructural transformations of the slag in the presence of 20 wt% sintered magnesia for preparation of refractory materials was experimentally determined based on the XRD and SEM–EDS analyses.

Figure 5.30 shows the XRD patterns of the refractory materials obtained by sintering at 1350 °C for different periods of time. When the sintering time was 1 h, the main phases of the sample were forsterite, magnesium chromate spinel, magnesium aluminate spinel and enstatite. However, when the time was extended to 2 h, 3 h, 4 h, and 5 h, the main phases the sintered samples were still forsterite, magnesium chromate spinel, magnesium aluminate spinel and enstatite. It showed that by fixing the addition of magnesia of 20 wt% and sintering temperature of 1350 °C, magnesium oxide could completely react with the main components in the slag in a short time to produce forsterite, spinel, and enstatite.

Figures 5.31, 5.32, 5.33, and 5.34 show the SEM–EDS results of sample 1 (20 wt% sintered magnesia, 1350 °C, 1 h), sample 2 (20 wt% sintered magnesia, 1350 °C, 2 h), sample 3 (20 wt% sintered magnesia, 1350 °C, 4 h), and sample 4 (20 wt% sintered magnesia, 1350 °C, 5 h), respectively. By comparing the EDS results in Figs. 5.31, 5.32, 5.33 and 5.34, it was found that with the extension of sintering time, the MgO content in both spinel and forsterite increased while that in the silica-rich phase decreased. It revealed that as the sintering time increased, magnesium oxide reacted with free silica to form forsterite and reacted with iron oxide, chromium oxide

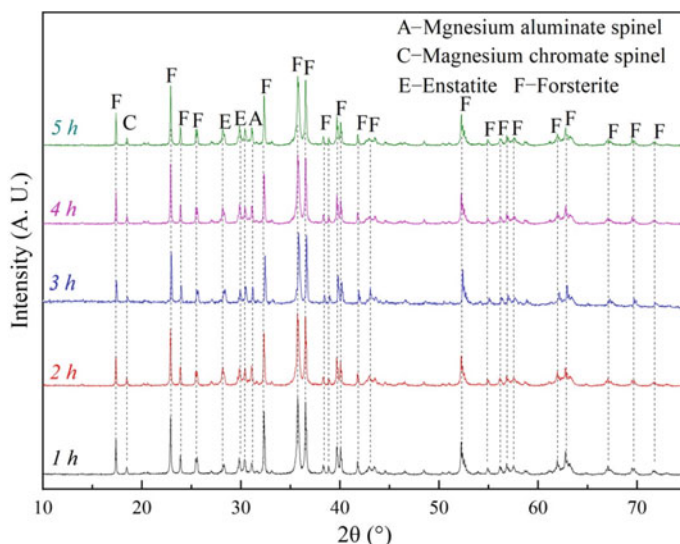


Fig. 5.30 XRD patterns of the refractory materials obtained by sintering for different periods of time

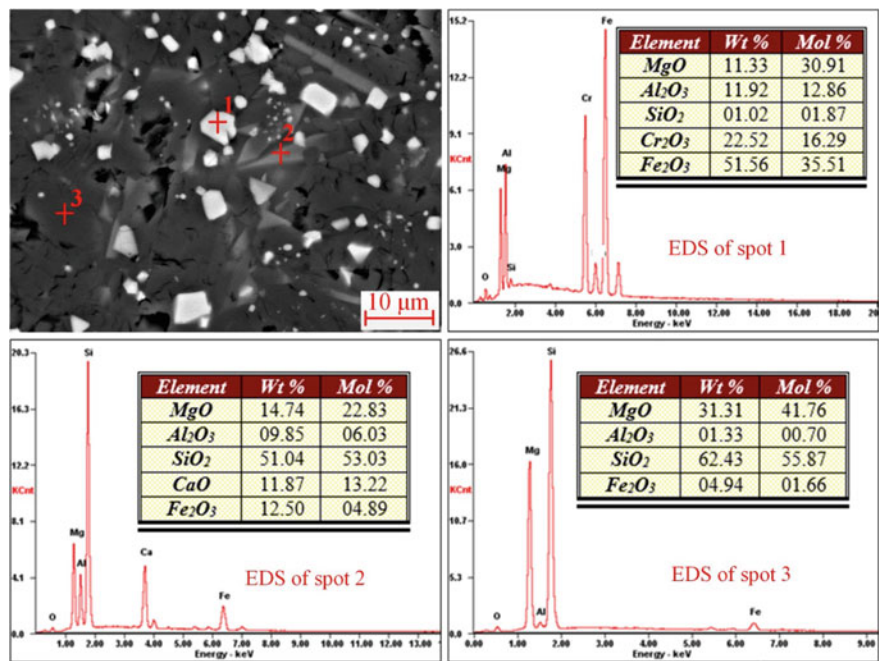


Fig. 5.31 SEM–EDS analysis of the refractory material obtained by sintering for 1 h

and aluminum oxide to produce more spinel. In addition, the SEM results indicated that increasing sintering time was beneficial to the growth of spinel particles.

As shown in Fig. 5.35, when the sintering time varied from 1 to 5 h, all the refractory material had refractoriness exceeding 1600 °C. Obviously, the sintering time had a relatively weak effect on the refractoriness of the refractory material.

The effects of sintering time on the bulk density, apparent porosity, and compressive strength of the refractory material were evaluated under the same sintering conditions, as shown in Fig. 5.36. As the sintering time increased from 1 to 4 h, the bulk density of the refractory material increased from 2.83 to 2.94 g/cm³. Meanwhile, the apparent porosity decreased from 6.92% to 1.44%. The compressive strength increased from 77.69 MPa to 108.09 MPa. As the sintering time was further prolonged, the bulk density and compressive strength of the refractory material decreased gradually. As expected, the changing tendency of apparent porosity was opposite to the variations of bulk density and compressive strength.

The effect of sintering time on the hydration resistance of the refractory material was evaluated under the same sintering conditions, as shown in Table 5.14. When the sintering time varied from 1 to 5 h, the mass increase percentage of the refractory material changed slightly. All the examined refractory materials had good resistance to hydration.

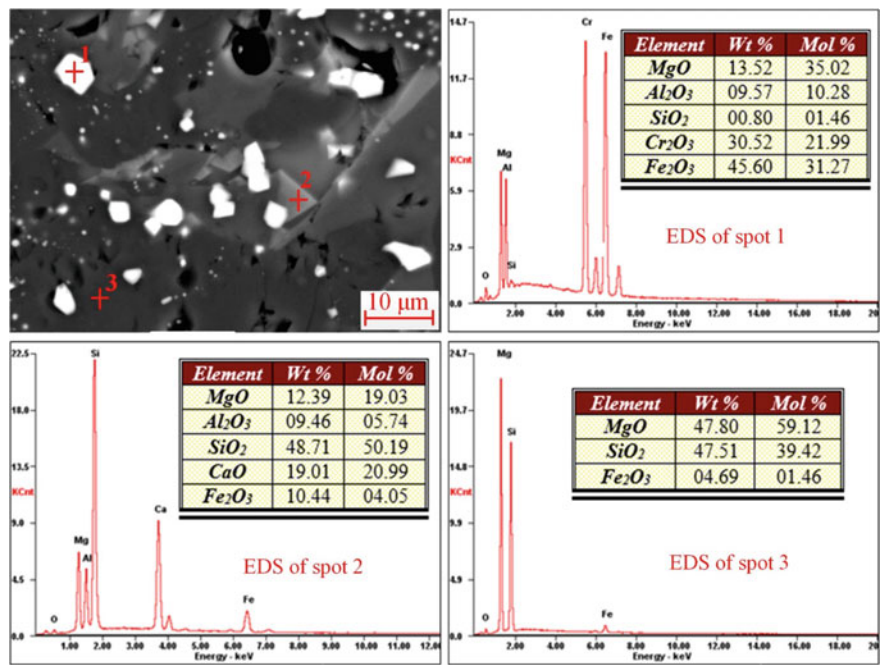


Fig. 5.32 SEM–EDS analysis of the refractory material obtained by sintering for 2 h

The thermal shock resistances of the refractory materials are shown in Table 5.15. When the sintering time increased from 1 to 5 h, the thermal shock resistance of the refractory material changed slightly within the cycles of 3–4.

Considering the effects of sintering time on the bulk density, apparent porosity, compressive strength, hydration resistance, and thermal shock resistance of the refractory material, the appropriate sintering time was 3 h.

The above results demonstrated that a good refractory material with refractoriness of 1660 °C, bulk density of 2.92 g/cm³, apparent porosity of 1.82%, compressive strength of 100.61 MPa, mass increase percentage of 0.004%, and thermal shock resistance of 4 cycles was obtained when the ferronickel slag was sintered at 1350 °C for 3 h with the addition of 20 wt% sintered magnesita. According to the Chinese National Refractory Material Production Standard (GB/T 2275–2007), the refractory material obtained was superior to commercial refractory materials (magnesite brick trademarks M-93, M-91, M-89, and M-87).

5.3.2.4 Effect of Chromium Oxide

The phase transformation of ferronickel slag in the presence of sintered magnesita (20 wt%) and chromium oxide during the sintering process was experimentally determined by investigating the effect of addition of chromium oxide varying from 0 wt%

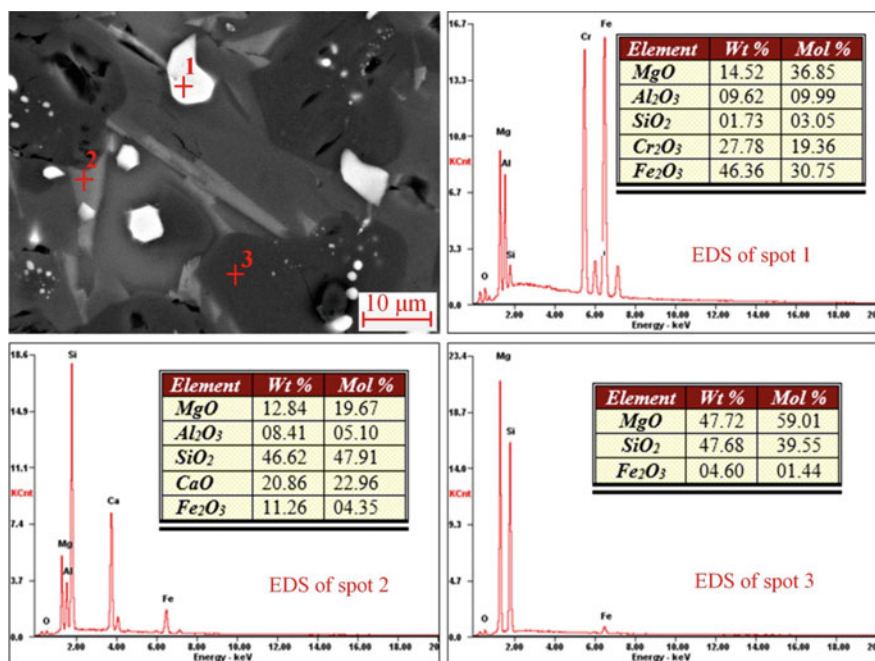


Fig. 5.33 SEM-EDS analysis of the refractory material obtained by sintering for 4 h

to 10 wt% at 1350 °C for 3 h. The obtained refractory materials were characterized by XRD and electron probe micro-analysis (EPMA).

Figure 5.37 shows the XRD patterns of the refractory materials sintered with different additions of chromium oxide. The main phases of the refractory materials in the absence of chromium oxide were forsterite, magnesium chromate spinel, magnesium aluminate spinel, and enstatite. As the addition of chromium oxide increased to 4 wt%, the magnesium chromate spinel disappeared, replaced by donathite ($\text{MgFe}_{0.2}\text{Cr}_{1.8}\text{O}_4$). As the addition of chromium oxide increased to 6 wt%, the diffraction peaks of forsterite, donathite, magnesium aluminate spinel, and enstatite remained. When the addition of chromium oxide was further increased, more enstatite was formed. As shown in Fig. 5.38 which summarizes the relevant reactions, without addition of chromium oxide (0 wt% chromium oxide), the olivine in the slag decomposed to forsterite, Fe_2O_3 and SiO_2 . The MgO added would preferably react with SiO_2 , along with Cr_2O_3 and Al_2O_3 in the slag, forming $\text{MgSiO}_4/\text{MgSiO}_3$, MgCr_2O_4 and MgAl_2O_4 , respectively. In the presence of 4–6 wt% chromium oxide, the reactions between MgO and $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$ took place firstly, producing donathite instead of magnesium chromate spinel directly. This was followed by the reaction between MgO and Al_2O_3 in the slag, which caused the generation of magnesium aluminate spinel. Thereafter, SiO_2 had reaction with MgO, producing more Mg_2SiO_4 with a minor amount of MgSiO_3 . When the addition of chromium oxide exceeded 6 wt%, the above reactions continued. However, because of continuous addition of chromium

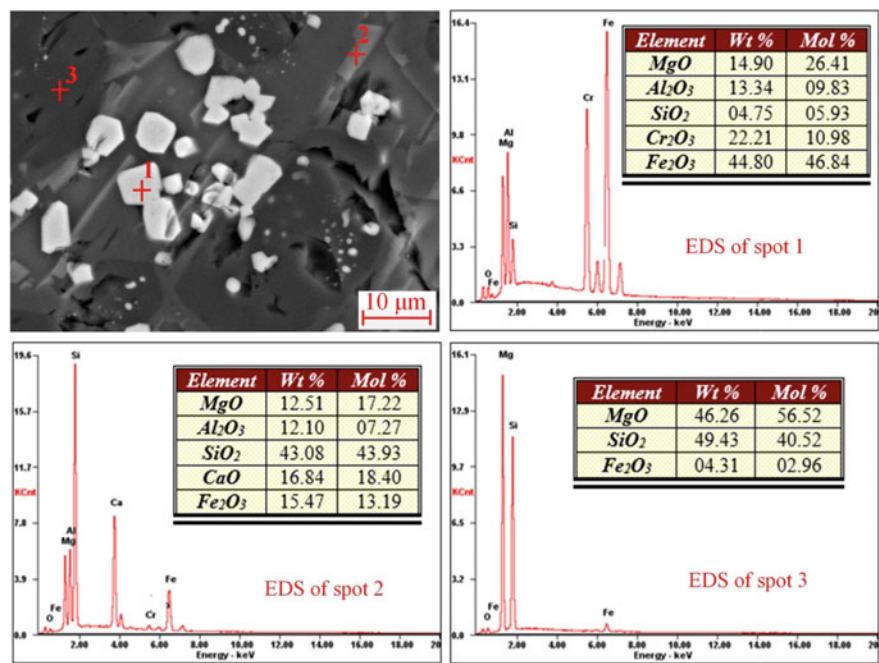


Fig. 5.34 SEM–EDS analysis of the refractory material obtained by sintering for 5 h

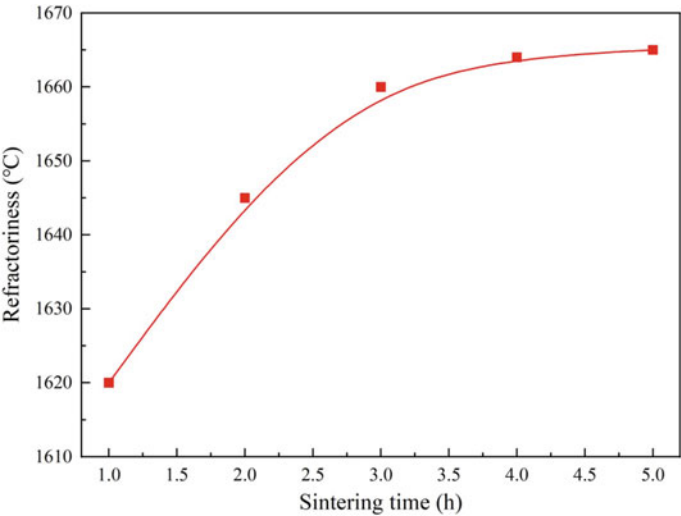


Fig. 5.35 Effect of sintering time on the refractoriness of the refractory material

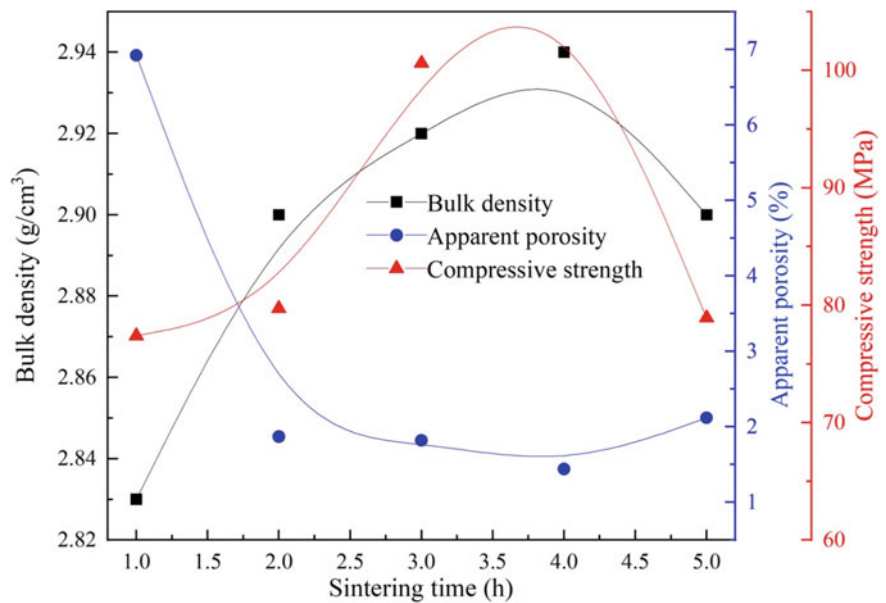


Fig. 5.36 Effects of sintering time on the bulk density, apparent porosity, and compressive strength of the refractory material

Table 5.14 Effect of sintering time on the mass increase percentage of the refractory material after hydration experiments

Sintering time (h)	1	2	3	4	5
Mass increase percentage (wt%)	0.003	0.002	0.004	0.005	0.002

Table 5.15 Effect of sintering time on the thermal shock resistance of the refractory material

Sintering time (h)	1	2	3	4	5
Cycle	3	4	4	3	3

oxide, more MgO was involved in the formation of spinel, mainly donathite. In other words, insufficient MgO had reaction with SiO₂ which would facilitate the formation of enstatite due to the reaction between the remnant SiO₂ and early formed forsterite. Obviously, the addition of chromium oxide could promote the generation of high-refractoriness phases, including donathite, magnesium aluminate spinel, and forsterite. However, its addition should be carefully controlled.

For verifying the above analysis, the morphologies and elemental distributions of Mg, Si, Cr, Fe, Al, and O in the refractory materials were examined by EPMA. The results of sample 1 (addition of 20 wt% magnesia, 0 wt% chromium oxide, 1350 °C, 3 h), sample 2 (addition of 20 wt% magnesia, 6 wt% chromium oxide, 1350 °C, 3 h),

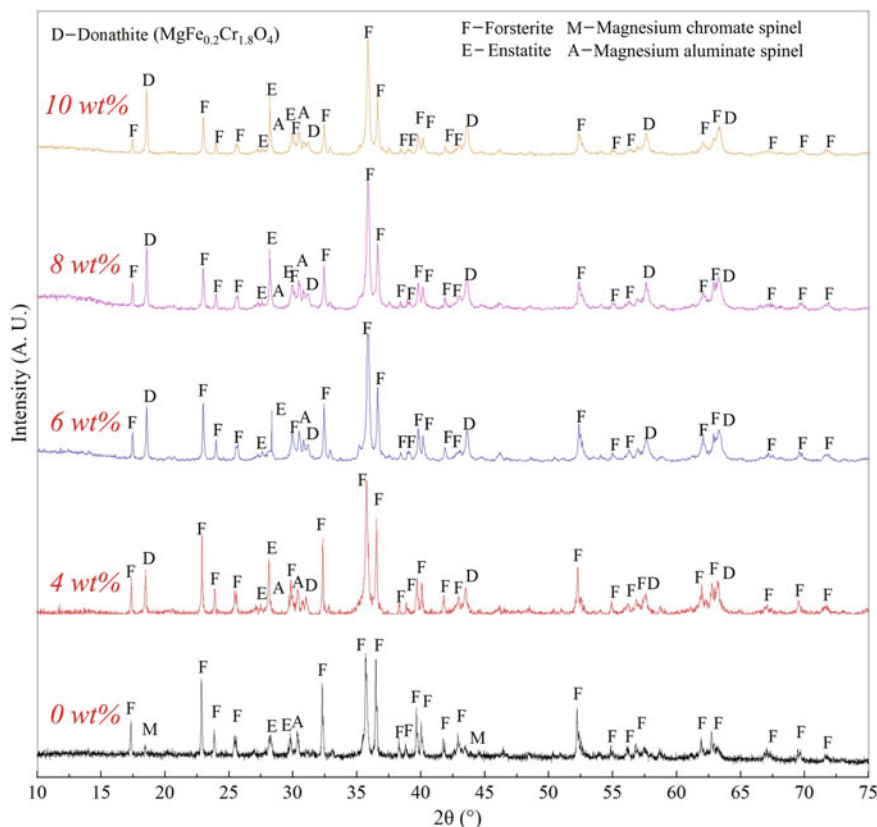


Fig. 5.37 XRD patterns of the refractory materials prepared by sintering with different additions of chromium oxide, reprinted from Ref. [26], copyright 2018, with permission from the American Chemical Society

and sample 3 (addition of 20 wt% magnesia, 10 wt% chromium oxide, 1350 °C, 3 h) are shown in Figs. 5.39, 5.40, and 5.41, respectively. The sample 1 had three different phases, namely forsterite, spinel, and a low-magnesium transient phase, as revealed by elemental distribution maps of Mg, Si, Cr, Fe, and Al in Fig. 5.39. According to the literature, the low-magnesium transient phase could change to spinel. It was confirmed by Figs. 5.6 and 5.7 in which with increasing addition of chromium oxide, the spinel phases significantly increased, while the low-magnesium transient phases decreased. By comparing Fig. 5.39 with Figs. 5.40 and 5.41, it was found that with increasing addition of chromium oxide, the distribution of Cr kept consistent with Fe, while the distributions of Si and Al agreed with that of Mg. It showed that in the presence of MgO and Cr₂O₃, the reaction between MgO, Cr₂O₃ and Fe₂O₃ initiated firstly, forming donathite, followed by the reaction between MgO and Al₂O₃ in the slag, which caused the generation of magnesium aluminate spinel. Then, SiO₂ reacted

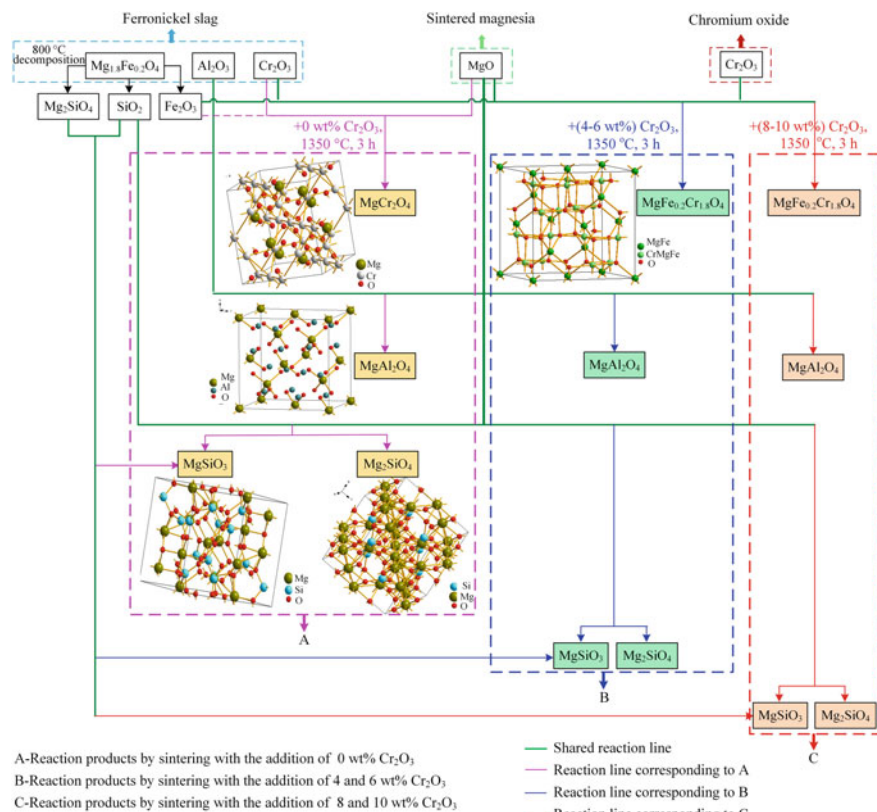


Fig. 5.38 Reactions involved in preparing refractory materials by sintering with different additions of chromium oxide, reprinted from Ref. [26], copyright 2018, with permission from the American Chemical Society

with MgO, producing forsterite or enstatite. These transitions were also consistent with the XRD patterns in Fig. 5.37.

The effect of chromium oxide addition on the refractoriness of refractory material was studied when the sample was sintered at 1350 °C for 3 h with the magnesia addition of 20 wt%. As shown in Fig. 5.42, when the addition of chromium oxide increased from 0 wt% to 6 wt%, the refractoriness of the refractory material increased from 1660 °C to 1840 °C. With further increase of the chromium oxide addition, the refractoriness decreased gradually. Evidently, there were two stages according to the changing trend of refractoriness. In the stage 1, forsterite remained as one of the main phases. Meanwhile, the amount of spinel phases, including donathite whose formation characterized the stage, increased continuously, which significantly enhanced the refractoriness of the refractory material. Therefore, in the presence of 6 wt% chromium oxide, the refractory material mainly composed of forsterite and spinel phases had a maximum refractoriness. In the stage 2 when the addition of chromium

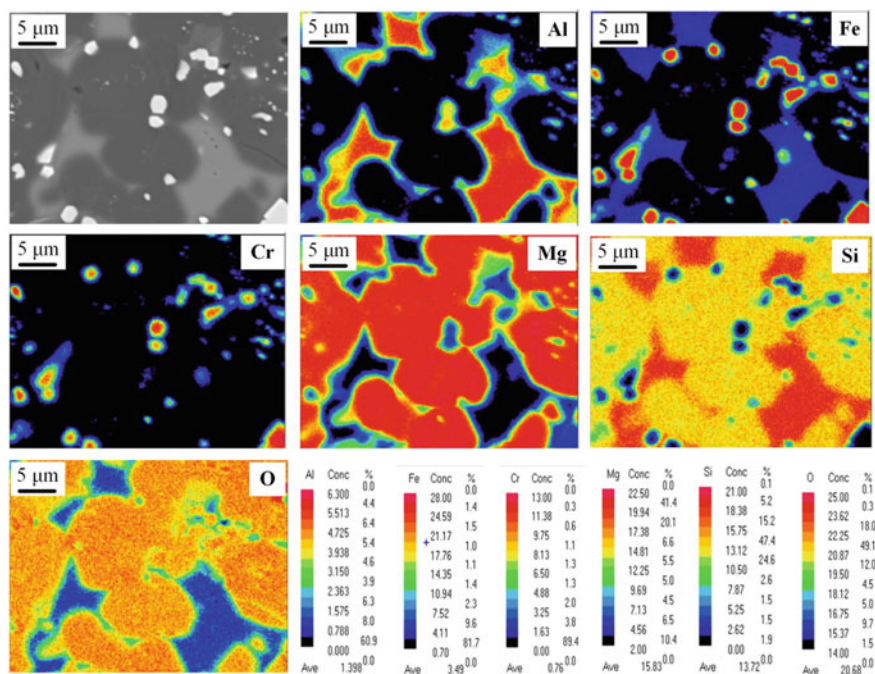


Fig. 5.39 EPMA analysis of the refractory material obtained by sintering with the addition of 0 wt% chromium oxide, reprinted from Ref. [26], copyright 2018, with permission from the American Chemical Society

oxide exceeded 6 wt%, as aforementioned, the amount of enstatite increased obviously. Because of the low eutectic temperature of forsterite and enstatite (1557 °C), the refractoriness of the refractory material decreased. These results demonstrated that the proper addition of chromium oxide promoted the formation of high melting point phases. However, excessive addition of chromium oxide was harmful to the preparation of refractory materials.

The effects of chromium oxide addition on the other properties of the refractory material, including bulk density, apparent porosity, and compressive strength, were also evaluated under the same conditions, as shown in Fig. 5.43. When the chromium oxide addition increased, the bulk density and the compressive strength of the refractory material decreased. On the contrary, the apparent porosity increased continuously with changes in the distribution of pores. In specific, as the addition of chromium oxide increased from 0 wt% to 10 wt%, the bulk density of refractory material decreased from 2.92 g/cm³ to 2.74 g/cm³ while the apparent porosity of refractory material increased from 1.82% to 18.47%. Simultaneously, the compressive strength of the refractory material decreased from 100.61 MPa to 82.9 MPa. Without doubt, these changes were closely associated with the phase transformation of the sample during sintering. The increase of chromium oxide addition promoted the formation of the spinel phases. The spinel phases inhibited the densification of

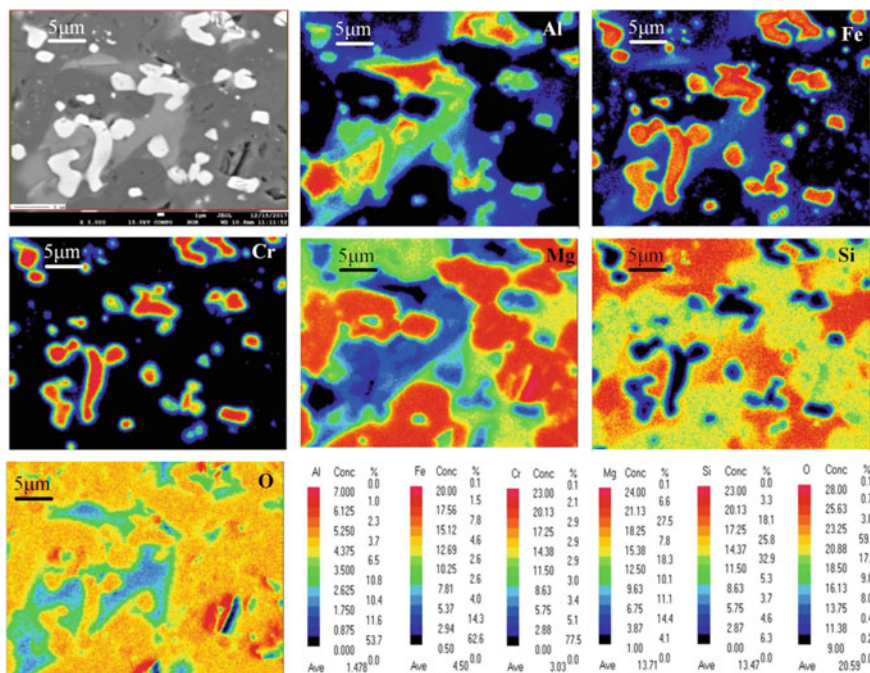


Fig. 5.40 EPMA analysis of the refractory material obtained by sintering with the addition of 6 wt% chromium oxide, reprinted from Ref. [26], copyright 2018, with permission from the American Chemical Society

the material because their recrystallization capacity is weak and their formation is accompanied with a large volume expansion. Meanwhile, as the chromium oxide addition increased, the liquid phase in the refractory material decreased, restraining the densification of the material.

The effect of chromium oxide addition on the hydration resistance of the refractory material was also evaluated under the same sintering conditions, as shown in Table 5.16. When the chromium oxide addition increased from 0 wt% to 10 wt%, the mass increase percentage of the refractory material changed slightly. All the refractory materials had good resistances to hydration.

The thermal shock resistances of the refractory materials obtained by sintering with different additions of chromium oxide are shown in Table 5.17. When the chromium oxide addition increased, the cycle of refractory material increased gradually. As the chromium oxide addition increased from 0 to 10 wt%, it increased from 4 to 7.

The effect of sintering temperature on the spinel formation and growth in the refractory material obtained with the addition of 20 wt% sintered magnesia and 6 wt% chromium oxide was revealed by the XRD, XPS, and SEM-EDS analyses.

As shown in Fig. 5.44, the phases of the refractory materials sintered at 1200 °C and 1300 °C were forsterite, periclase, enstatite, and spinel phases which included

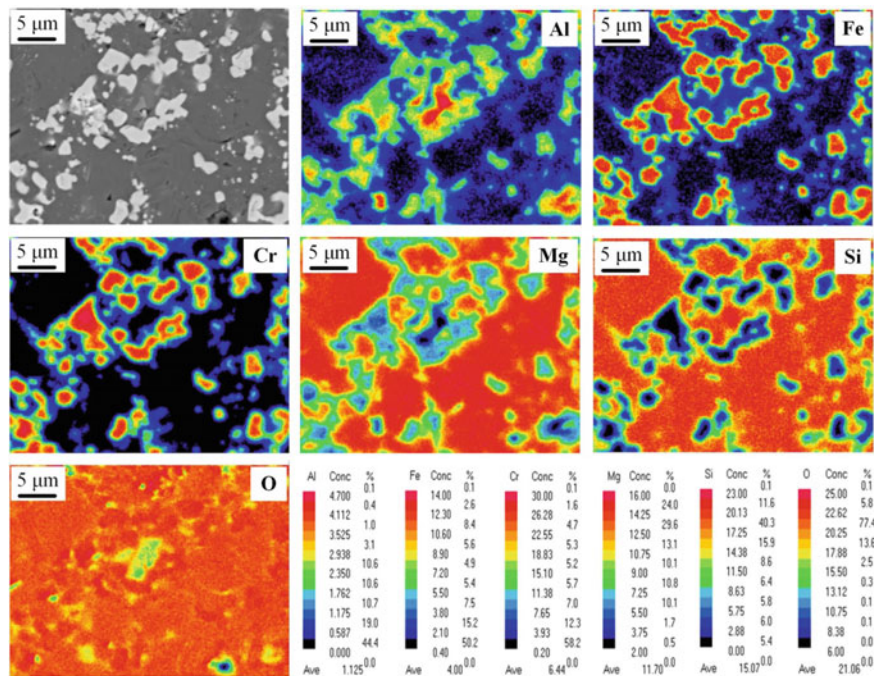


Fig. 5.41 EPMA analysis of the refractory material obtained by sintering with the addition of 10 wt% chromium oxide, reprinted from Ref. [26], copyright 2018, with permission from the American Chemical Society

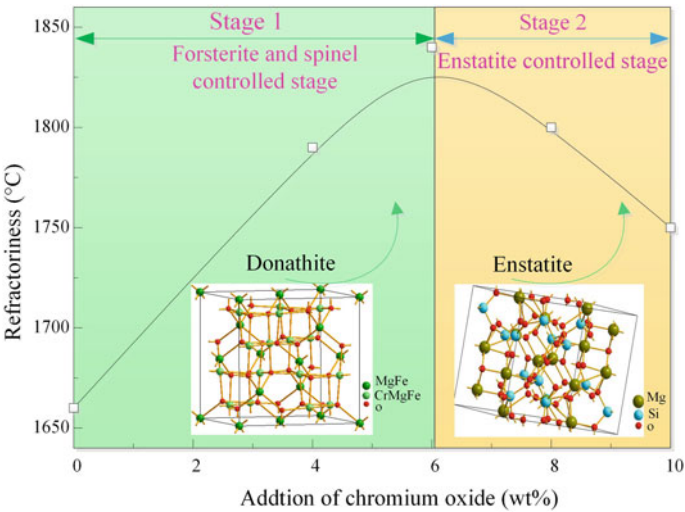


Fig. 5.42 Effect of chromium oxide addition on the refractoriness of the refractory material, reprinted from Ref. [26], copyright 2018, with permission from the American Chemical Society

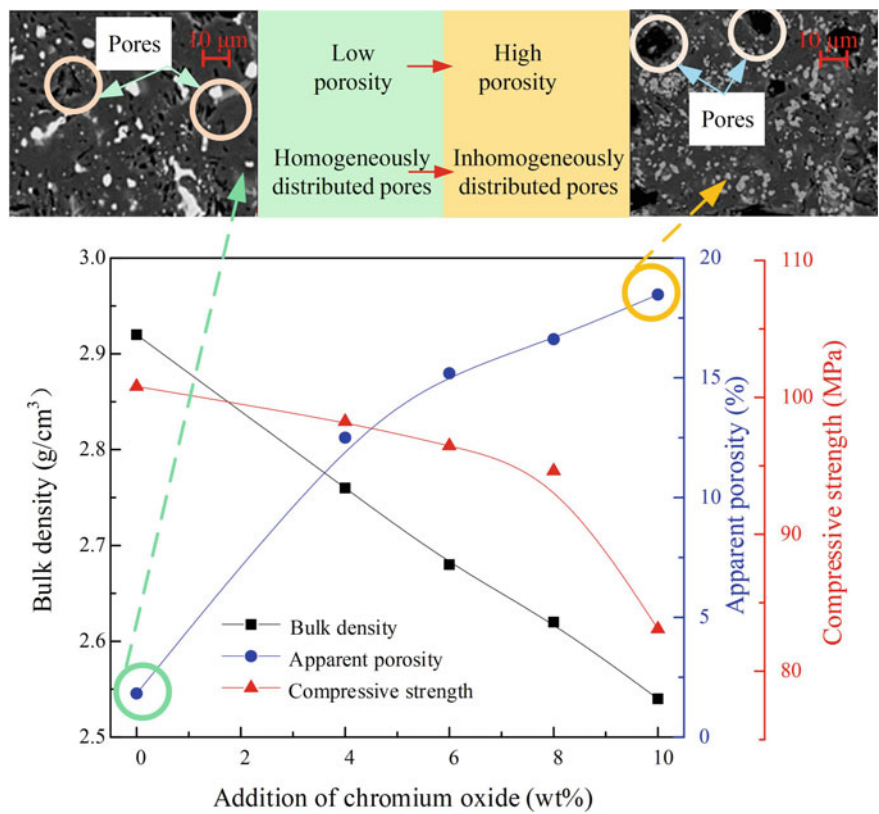


Fig. 5.43 Effect of chromium oxide addition on the bulk density, apparent porosity, and compressive strength of the refractory material, reprinted from Ref. [26], copyright 2018, with permission from the American Chemical Society

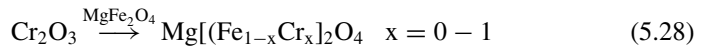
Table 5.16 Effect of chromium oxide addition on the mass increase percentage of the refractory material after hydration experiments

Chromium oxide addition (wt%)	0	4	6	8	10
Mass increase percentage (wt%)	0.0041	0.0017	0.0009	0.0007	0.0005

Table 5.17 Effect of chromium oxide addition on the thermal shock resistance of the refractory material

Chromium oxide addition (wt%)	0	4	6	8	10
Cycle	4	5	6	6	7

donathite ($\text{MgFe}_{0.2}\text{Cr}_{1.8}\text{O}_4$) and magnesium aluminate spinel. The formation of the spinel phases was a direct result of the addition of sintered magnesia which induced the reaction between MgO and Fe_2O_3 , Cr_2O_3 , and Al_2O_3 . The presence of diffraction peaks of periclase indicated that below 1300°C the reaction between magnesia and ferronickel slag was incomplete. At 1350°C , the periclase disappeared. As the temperature increased, the diffraction peaks of enstatite declined gradually and disappeared at 1500°C . It was ascribed to the increase of the silica-rich phase (glassy phase), which reduced the content of free silica in the system. This change was expected to contribute to a higher refractoriness of the refractory material as it could restrain the negative impact of formation of low melting point eutectic compound between forsterite and enstatite. Figure 5.44 also shows the presence of donathite throughout the temperature range of 1200 – 1500°C , which can be explained by Eqs. (5.27) and (5.28).



$$\Delta R = \frac{R(\text{Fe}^{3+}) - R(\text{Cr}^{3+})}{R(\text{Fe}^{3+})} \times 100\% \quad (5.29)$$

where ΔR represents the relative radius difference between Fe^{3+} and Cr^{3+} ions, and $R(\text{Fe}^{3+})$ and $R(\text{Cr}^{3+})$ denote the radii of Fe^{3+} and Cr^{3+} ions (0.0645 nm and 0.0615 nm), respectively. Because of the small difference between the radii of Fe^{3+}

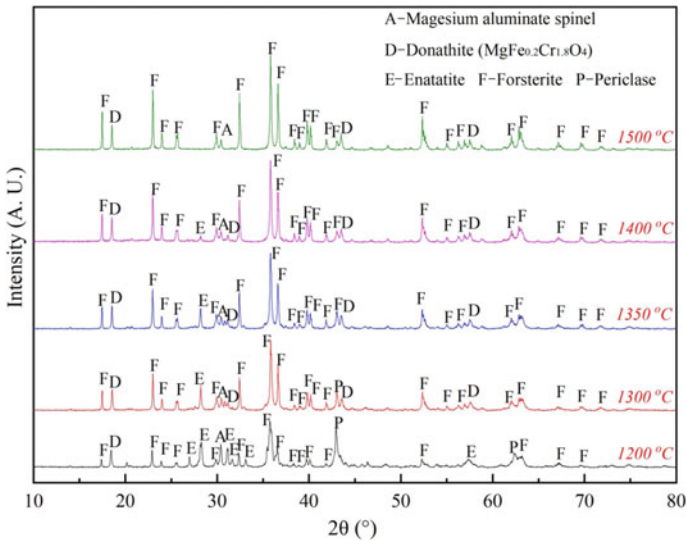


Fig. 5.44 XRD patterns of the refractory materials obtained by sintering at different temperatures in the presence of 20 wt% sintered magnesia and 6 wt% chromium oxide, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

and Cr^{3+} ions, ΔR was estimated to be only 4.65%. Hence, the replacement of Cr^{3+} ions in the formed spinel (MgCr_2O_4) by Fe^{3+} ions, which were released through decomposition of olivine, could proceed easily, thereby producing a solid spinel as donathite. In addition, the radius difference between Fe^{3+} and Cr^{3+} ions led to lattice distortion, which was beneficial to the grain growth of donathite. In other words, the reactions between magnesia and chromium oxide/iron oxide initiated first, resulting in formation of donathite instead of magnesium chromate spinel. Except for donathite, another minor spinel phase, magnesium aluminate spinel, was also observed in the entire temperature range due to the reaction between magnesia and alumina in the slag.

The XPS analysis of ferronickel slag, sample 1 (20 wt% sintered magnesia, 6 wt% Cr_2O_3 , 1200 °C, 3 h), sample 2 (20 wt% sintered magnesia, 6 wt% Cr_2O_3 , 1350 °C, 3 h) and sample 3 (20 wt% sintered magnesia, 6 wt% Cr_2O_3 , 1500 °C, 3 h) was performed to further explore the formation behavior of the main spinel phase, donathite, during the sintering process. Figure 5.45 shows the XPS wide spectra of ferronickel slag and samples 1–3. The atom contents of Fe and Cr of ferronickel slag were 3.16 at.% and 0.27 at.%, respectively, while those of Fe and Cr of sample 1 were 1.99 at.% and 1.22 at.%, respectively. Because of the same raw

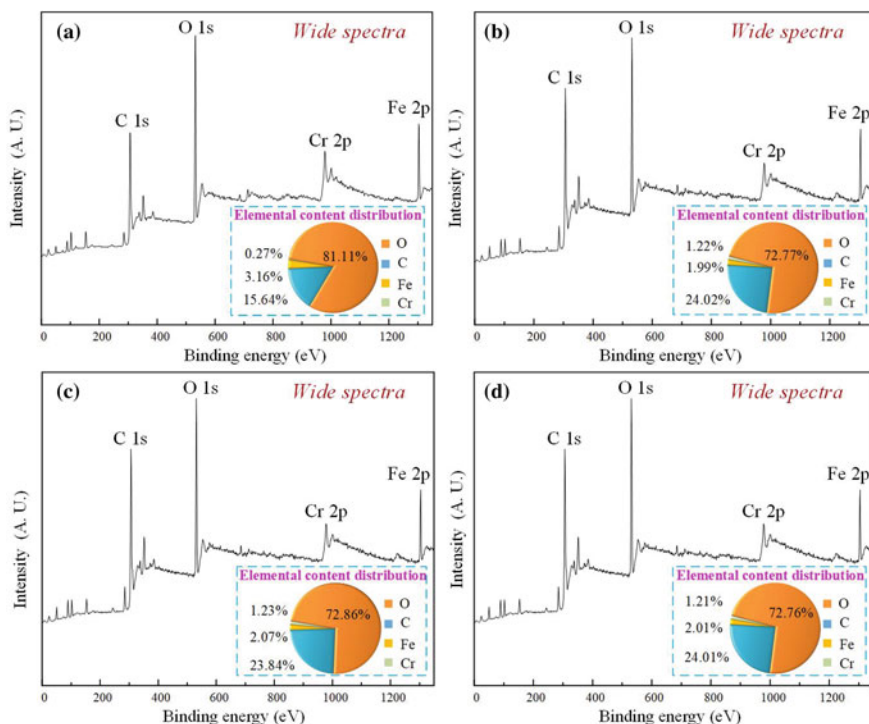


Fig. 5.45 XPS wide spectra of **a** ferronickel slag, **b** sample 1, **c** sample 2, and **d** sample 3, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

material, the atom contents of Fe and Cr on the surfaces of the samples changed slightly. Figure 5.46a shows the Fe2p regions in the spectra of ferronickel slag and samples 1–3, respectively. The photoelectron peaks at binding energies of 709.6 eV (Fe2p_{3/2}), 710.8 eV (Fe2p_{3/2}), and 712.8 eV (Fe2p_{3/2}) were ascribed to Fe²⁺ ions in the ferronickel slag³⁹. Owing to partial oxidization of the ferronickel slag during sintering, the Fe2p_{3/2} peak position for Fe³⁺ ions was found at 714.8 eV and a Fe³⁺ satellite was found at 714.2 eV (Fe2p_{3/2}). The photoelectron peaks at binding energies of 712.6 eV (Fe2p_{3/2}) and 715.5 eV (Fe2p_{3/2}) were attributed to Fe³⁺ ions in the donathite of sample 1. Meanwhile, the Fe2p_{3/2} peaks for Fe²⁺ ions located at 709.3 eV and 710.7 eV were attributed to incomplete reaction of the slag at the low sintering temperature. In sample 2, the Fe2p_{3/2} peaks for Fe³⁺ were found at 710.5 eV and 713.3 eV. Because of the rapid formation of the liquid phases at the high sintering temperature, a peak for Fe²⁺ ions was discovered at 709.6 eV (Fe2p_{3/2}) in sample 3. Figure 5.46b shows the Cr2p regions in the spectra of ferronickel slag and sample 1–3. Due to the low atom content of Cr in the ferronickel slag (0.27 at.%), the Cr2p region was absent in the spectra of ferronickel slag. However, in sample 1, the photoelectron peaks at binding energies of 576.4 eV (Cr2p_{3/2}) and 576.9 eV (Cr2p_{3/2}) were ascribed to the Cr³⁺ ions in the donathite of the refractory material. The Cr2p_{3/2} peak for Cr²⁺ ions at 575.5 eV indicated the possible replacement of some Cr²⁺ ions by Fe²⁺ ions which resulted in the formation of donathite. With increasing sintering temperature, there was no change of the valence of Cr in the refractory materials. According to the above analysis, Cr was believed to be stabilized as Cr³⁺ in the donathite without toxicity. Meanwhile, the replacement of Cr³⁺ ions by Fe³⁺ ions in the octahedral vacancies of magnesium chromate spinel promoted the formation of donathite, which would further stabilize Cr in the refractory materials.

The microstructural evolutions of the samples obtained at different sintering temperature in the presence of 20 wt% sintered magnesia and 6 wt% chromium oxide were examined to explore growth behavior of the spinel phases. Figures 5.47, 5.48 and 5.49 show the SEM–EDS analyses of sample 1, sample 2, and sample 3, respectively. As shown in Fig. 5.47, the main phases of sample 1 were forsterite, spinel, enstatite and periclase. The spinel phase (spot 1 in Fig. 5.47) was located at the rims of enstatite grains and the forsterite was surrounded by enstatite (spot 2 in Fig. 5.47). The unreacted periclase (spot 3 in Fig. 5.47) was distributed randomly. According to Fig. 5.48, as the sintering temperature increased to 1350 °C, the periclase phase in sample 2 disappeared, while the glassy phase was observed. The spinel phases were distributed in the forsterite matrix which was connected by the glassy phase, producing a dense microstructure. From Figs. 5.47, 5.48 and 5.49, as the sintering temperature increased, the particle size of spinel increased significantly. Meanwhile, the contents of Fe₂O₃ in the spinel phases increased gradually. It indicated that elevating sintering temperature facilitated the formation of donathite.

According to Figs. 5.47, 5.48, and 5.49, the microstructural evolutions of the samples were dominated by the crystallization of spinel which increased significantly with sintering temperature. To quantify the changes, the growth of the particle size of spinel was characterized by determining its particle size distribution and average particle size. Figure 5.50 shows that the particle size of spinel in sample 1 varied

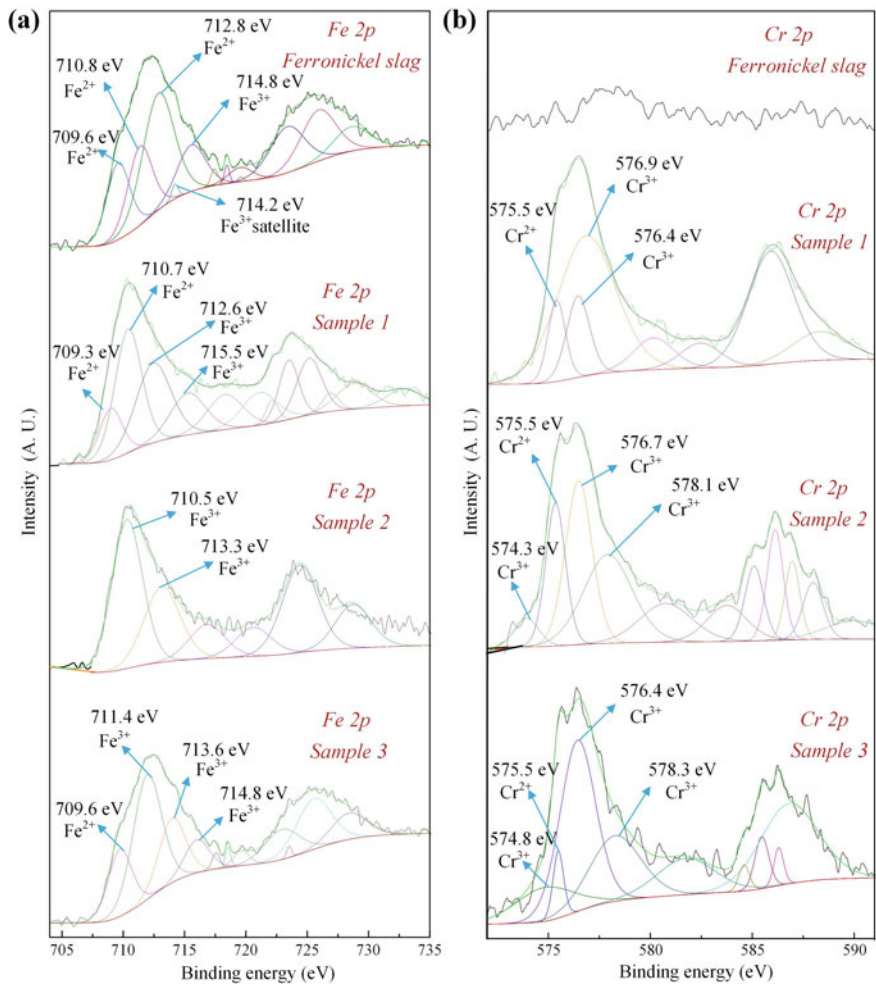


Fig. 5.46 **a** Fe2p regions and **b** Cr2p regions in the wide spectra of ferronickel slag, sample 1, sample 2, and sample 3, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

from 0 to 1 μm , while those in sample 2 and sample 3 were mainly distributed in the ranges up to 5 μm . The average spinel particle size was found to increase rapidly from 0.43 μm to 1.53 μm as the temperature increased from 1200 $^{\circ}\text{C}$ to 1350 $^{\circ}\text{C}$, and then to 2.79 μm at 1500 $^{\circ}\text{C}$. Evidently, in the presence of sintered magnesia and chromium oxide, increasing sintering temperature significantly promoted spinel formation and growth during preparation of refractory materials from ferronickel slag.

As shown in Fig. 5.51, the spinel formation and growth could be divided into two stages. In the first stage (stage I), the olivine in the slag was converted to forsterite,

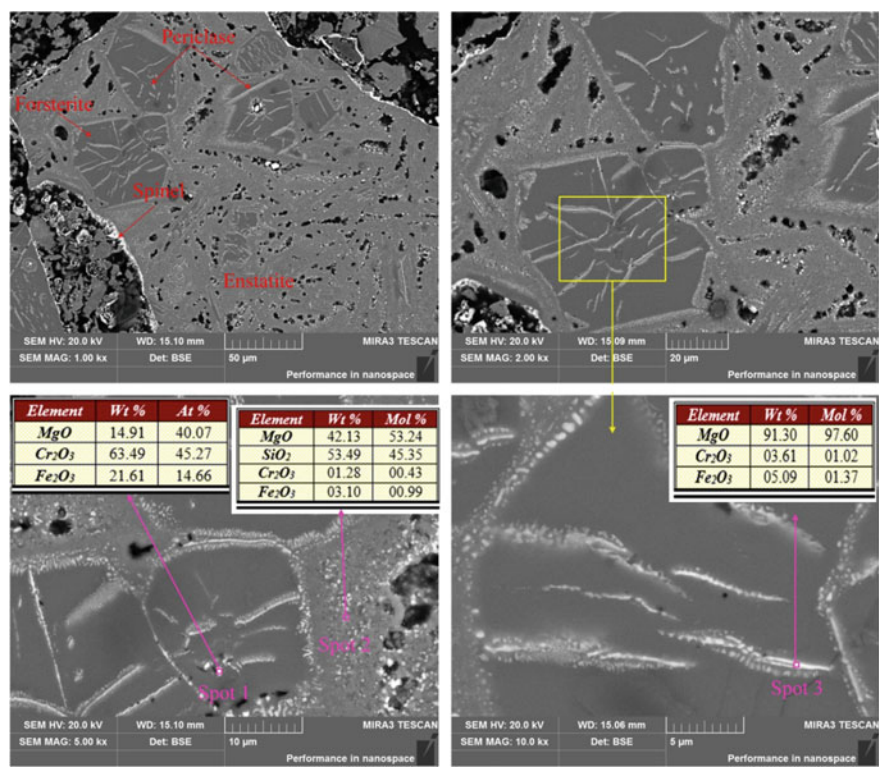


Fig. 5.47 SEM–EDS analysis of sample 1, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

iron oxide, and silica, producing the liquid phase that would improve densification of the material. In the second stage (stage II), the reaction between magnesia, chromium oxide, and iron oxide took place, producing donathite via the replacement of Cr^{3+} ions by Fe^{3+} ions in the octahedral vacancies of magnesium chromate spinel where chromium was stabilized in its nontoxic trivalent form. Meanwhile, the reaction between magnesia and alumina produced magnesium aluminate spinel. There were also partial dissolutions of alumina and calcium oxide (from the slag) in the liquid phase, promoting mass transfer and thus growth of donathite and forsterite grains. In addition, during the cooling process, the liquid phase was transformed to the glassy phase which bound the refractory components formed in the process. These transformations were expected to play an important role in elevating properties of the resulting refractory material.

The effect of sintering temperature on the properties of the refractory material was investigated by fixing the magnesia addition of 20 wt% and chromium oxide addition of 6 wt%.

The variation of refractoriness of the slag-derived refractory material with sintering temperature is illustrated in Fig. 5.52. It was demonstrated that the

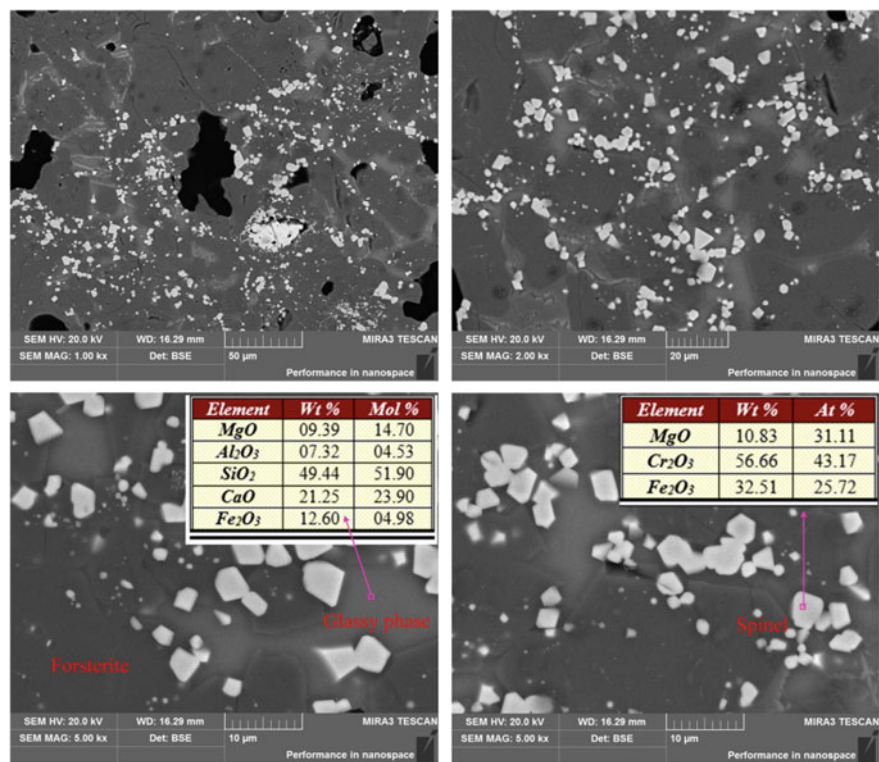


Fig. 5.48 SEM–EDS analysis of sample 2, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

refractoriness of the refractory material increased linearly from 1730 °C to 1840 °C ($Y = 0.73X + 850$ where Y and X denote refractoriness and temperature, respectively) when sintering temperature increased from 1200 °C to 1350 °C. As the sintering temperature increased further to 1500 °C, the refractoriness showed an increase of only 30 °C. Obviously, the changing trend could be divided into two stages (Fig. 5.52). In stage 1 up to 1350 °C, the chemical activity of the magnesia increased with increasing sintering temperature, resulting in continuous formation of spinel phases (donathite and magnesium aluminate spinel) and forsterite which improved the refractoriness of the refractory material obviously. When the sintering temperature was higher than 1350 °C (stage 2), the spinel phases grew rapidly. Meanwhile, the quantity of enstatite decreased gradually, inhibiting formation of its eutectic compound with forsterite. Hence, the refractoriness of the refractory material increased continuously.

The variations of the bulk density, apparent porosity, and compressive strength of the refractory material with sintering temperature are shown in Fig. 5.53. As the sintering temperature increased, the bulk density and compressive strength of the refractory material increased considerably. On the contrary, the apparent porosity

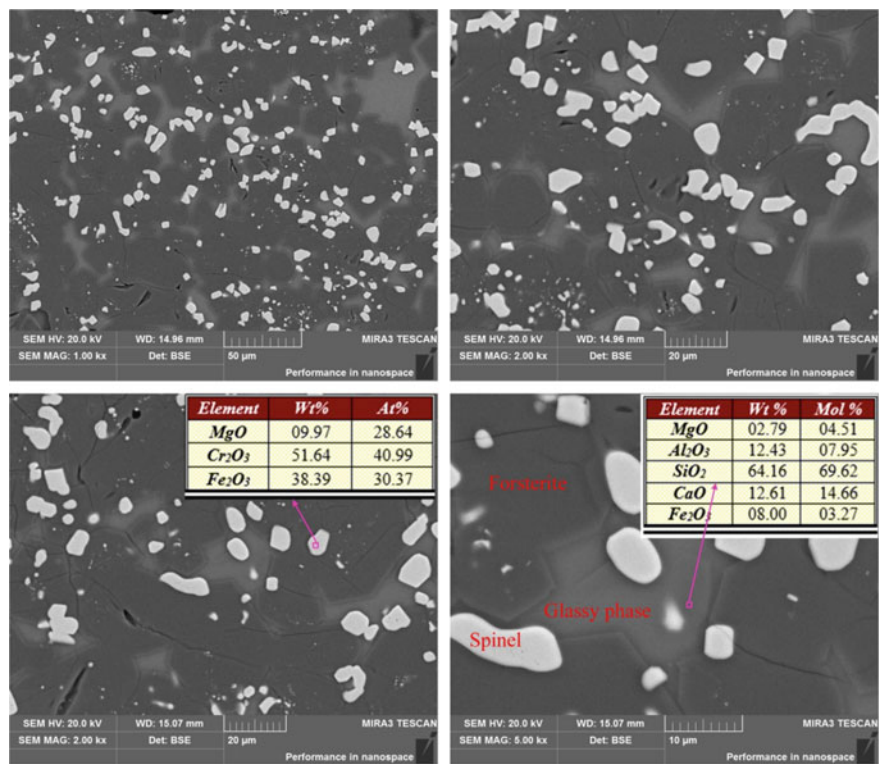


Fig. 5.49 SEM-EDS analysis of sample 3, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

decreased gradually. Specifically, as the sintering temperature varied from 1200 °C to 1350 °C, the bulk density of refractory material increased by 0.33 g/cm³ and the compressive strength increased by 57.64 MPa. Meanwhile, the apparent porosity decreased by 14.96%. When the sintering temperature increased further, those properties of the refractory material changed slightly. Evidently, these properties were in a close relationship with formation and growth of spinel and forsterite particles, as well as the generation of glassy phase which was evolved from enstatite, causing a dense microstructure.

The effect of sintering temperature on the hydration resistance of the refractory material obtained by sintering with the additions of 20 wt% sintered magnesia and 6 wt% chromium oxide was evaluated under the same sintering conditions, as shown in Table 5.18. When the sintering temperature increased from 1200 °C to 1300 °C, the mass increase percentage of the refractory material decreased from 0.042 wt% to 0.0047 wt%. As the sintering temperature further increased, the mass increase percentage decreased slightly.

The thermal shock resistances of the refractory materials are shown in Table 5.19. When the sintering temperature increased, the thermal shock resistance of the

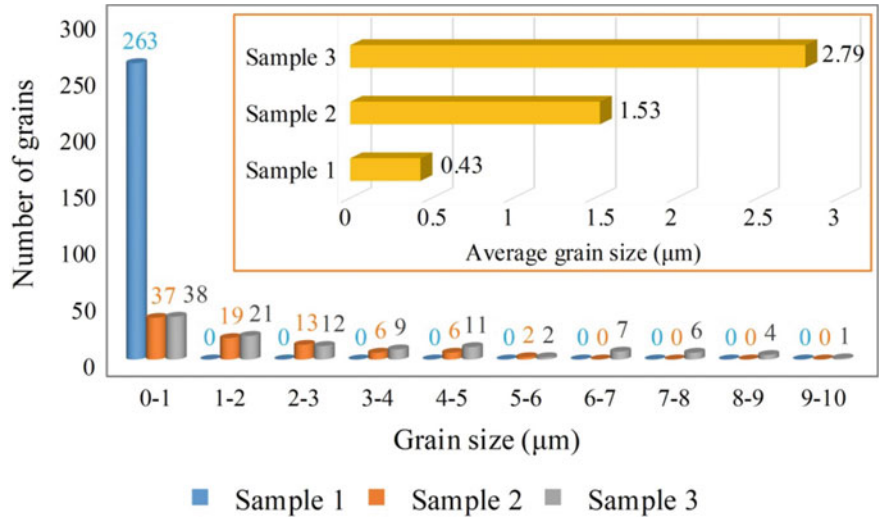


Fig. 5.50 Particle size distributions and average particle sizes of spinels in sample 1, sample 2, and sample 3, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

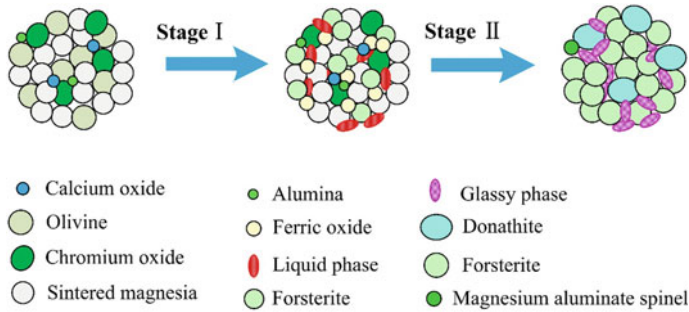


Fig. 5.51 Schematic illustration of phase transformations and microstructural evolutions of the refractory material, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

refractory material increased gradually. When the sintering temperature increased from 1200 to 1500 °C, it increased from 3 to 7 cycles.

The above analyses showed that a great refractory material could be obtained by selecting a suitable sintering temperature with the addition of chromium oxide due to its strong impact on the spinel formation and growth of the material during the sintering process. For example, after sintering at 1350 °C, the material had refractoriness of 1840 °C, bulk density of 2.68 g/cm³, apparent porosity of 15.19% and compressive strength of 96.28 MPa, respectively. This kind of refractory material,

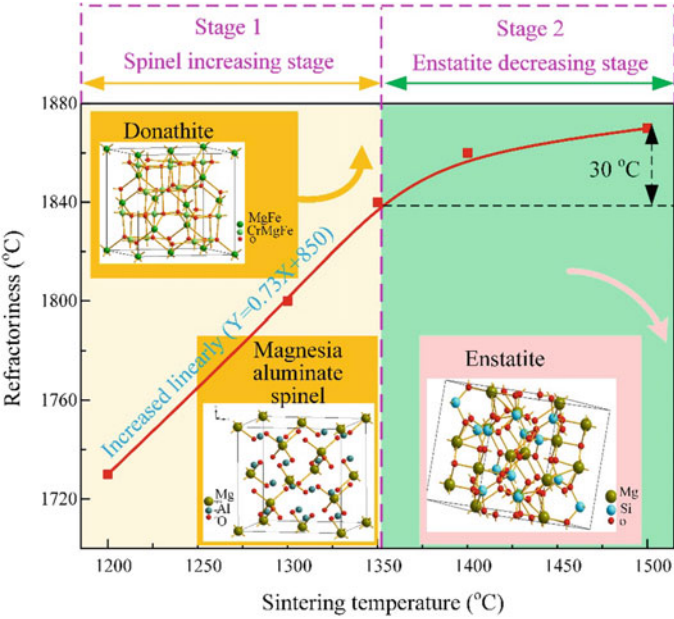


Fig. 5.52 Effect of sintering temperature on the refractoriness of the refractory material, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

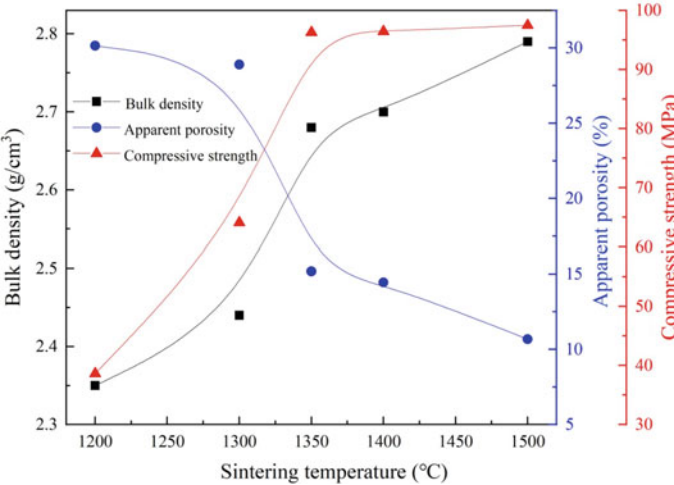


Fig. 5.53 Effect of sintering temperature on the bulk density, apparent porosity, and compressive strength of the refractory material, reprinted from Ref. [27], copyright 2020, with permission from the American Ceramic Society

Table 5.18 Effect of sintering temperature on the mass increase percentage of the refractory material obtained by sintering with the additions of 20 wt% sintered magnesia and 6 wt% chromium oxide after hydration experiments

Sintering temperature (°C)	1200	1300	1350	1400	1500
Mass increase percentage (wt%)	0.042	0.0047	0.0009	0.00087	0.00085

Table 5.19 Effect of sintering time on the thermal shock resistance of the refractory material obtained by sintering with the additions of 20 wt% sintered magnesia and 6 wt% chromium oxide

Sintering temperature (°C)	1200	1300	1350	1400	1500
Cycle	3	4	6	6	7

featured by high amounts of forsterite and spinel phases, showed good comprehensive properties that meet requirements of many high-temperature applications [34].

5.3.2.5 Industrial Test

According to the optimized process parameters obtained in the laboratory, an industrial production test was carried out in a refractory plant by sintering of ferronickel slag with the addition of sintered magnesia in Henan, China. A refractory material was obtained with refractoriness of 1660 °C, bulk density of 2.71 g/cm³, apparent porosity of 17.39%, compressive strength of 100.61 MPa, and mass increase percentage of 0.004% (Fig. 5.54). The comparison between this technology and the traditional technology for preparation of forsterite refractory materials is given in Table 5.20. This technology uses solid waste (ferronickel slag) as the raw material and does not require prior calcination. Compared with the traditional method, the required sintering temperature in this technology can be decreased from 1500–1550 °C to 1350 °C. The comprehensive performance of the material is better than the same type of commercial products. It has a good application prospect.

Table 5.20 Comparison between the traditional technology and this technology for producing forsterite refractory materials

	Traditional technology	This technology
Main raw materials	Peridotite, serpentine, etc. (mineral resources)	Ferronickel slag (waste) and sintered magnesia
Raw material pretreatment	Calcination required	No calcination required
Sintering temperature	1500–1550 °C	1350 °C
Sintering time	3–6 h	3 h
Product properties	Refractoriness of 1650 °C, bulk density of 2.65 g/cm ³ , and apparent porosity of 19%	Refractoriness of 1660 °C, bulk density of 2.71 g/cm ³ , and apparent porosity of 17.39%



Fig. 5.54 Photos of the refractory bricks obtained from industrial-scale test

5.4 Preparation of Lightweight Thermal Insulation Materials from Ferronickel Slag

Based on preparation of forsterite refractory materials from ferronickel slag, it was further proposed to prepare thermal insulation material using ferronickel slag by taking advantage of the thermal decomposition characteristics of additives (such as magnesite) to achieve low density. At the same time, small amounts of lightweight refractory pore-forming agent and organic binder were added to strengthen the comprehensive performance of high-temperature lightweight insulation materials. Specifically, the former could not only effectively increase the porosity of the material with lower bulk density, but also promote the refractory performance. The latter has good dispersibility, easy volatility, and can optimize microscopic pores. The microporosity of the material could be increased without affecting the crystal phase transformation during the high temperature processing of the material, which would further ensure the thermal insulation effect of the material. Thus, using magnesite as a refractory additive and fly ash cenosphere (FAC) as a pore-forming agent,

Table 5.21 Main chemical composition of FAC

Component	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	K ₂ O	TiO ₂	CaO	MgO	LOI
Content (wt%)	27.39	52.06	2.29	1.37	1.09	0.67	0.60	14.25

Table 5.22 Main chemical composition of magnesite

Component	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	LOI
Content (wt%)	2.57	7.59	0.94	2.07	46.80	40.32

ferronickel slag can be used to prepare high-temperature lightweight thermal insulation materials. The main chemical compositions of FAC and magnesite are shown in Tables 5.21 and 5.22, respectively.

Initially, the grounded ferronickel slag (86 wt% of the particles passing 74 μm sieve), FAC and magnesite (89 wt% of the particles passing 74 μm sieve) were carefully mixed. A few briquettes of 20 mm in diameter and 20 mm in height were produced by manual hydraulic pressing at 20 MPa using 5 wt% magnesium chloride solution (1.3 g/cm³) as the binder. The briquettes were then dried in a vacuum drying oven at 105 °C for 4 h. After drying, the briquettes were placed in a muffle furnace for sintering. After sintering at designated temperatures for given periods of time, the briquettes were cooled to room temperature and then taken out for the subsequent characterization tests.

5.4.1 Effect of FAC Addition

The effect of FAC addition on the bulk density, apparent porosity, compressive strength, thermal conductivity, and refractoriness of the sample was studied after sintering at 1100 °C for 3 h with the magnesite addition of 15 wt%. As shown in Fig. 5.55, when the addition of FAC increased from 30 wt% to 60 wt%, the bulk density of the sample decreased from 1.26 g/cm³ to 0.93 g/cm³. Meanwhile, the apparent porosity increased from 35.31% to 36.35% and the compressive strength decreased from 2.74 MPa to 1.82 MPa. According to Figs. 5.56 and 5.57, as the addition of FAC increased, the thermal conductivity and refractoriness of the sample decreased gradually. In specific, when the addition of FAC increased from 30 wt% to 60 wt%, the thermal conductivity of the samples decreased from 0.3453 W/(m·K) to 0.3045 W/(m·K) and the refractoriness decreased from 1351 °C to 1275 °C. Thus, the suitable addition of FAC was 50 wt%.

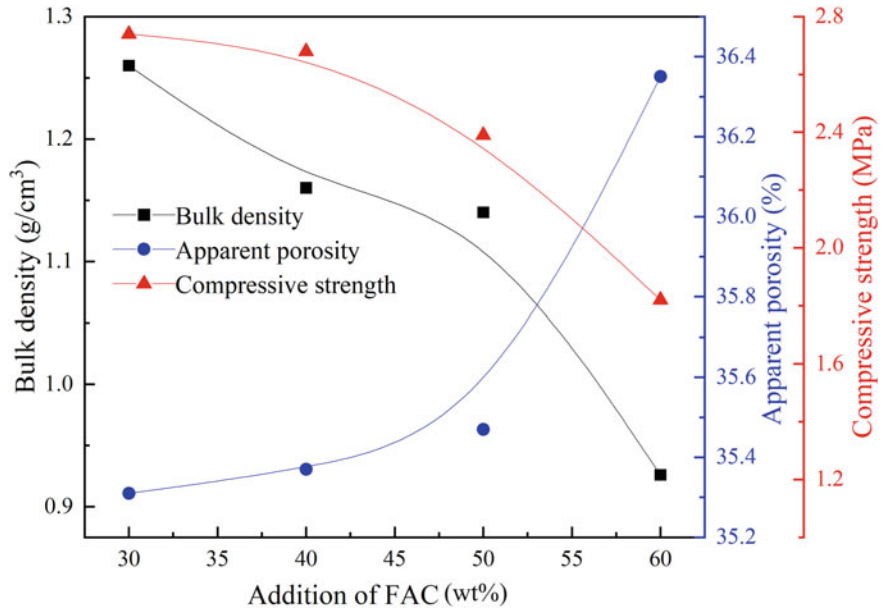


Fig. 5.55 Effects of FAC addition on the bulk density, apparent porosity, and compressive strength of the sample

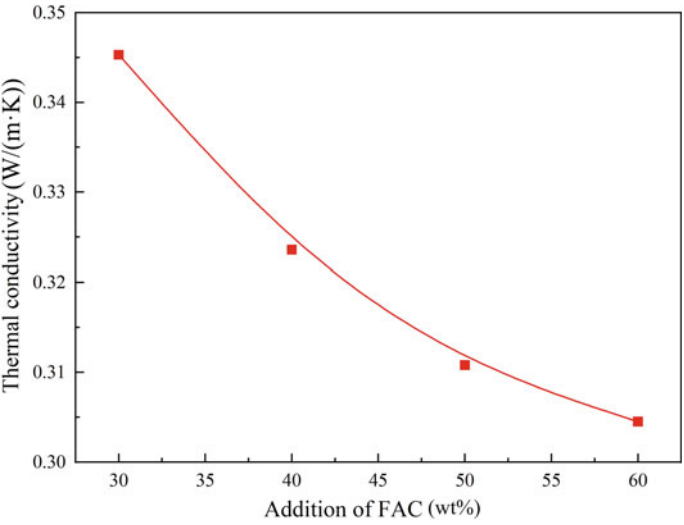


Fig. 5.56 Effect of FAC addition on the thermal conductivity of the sample

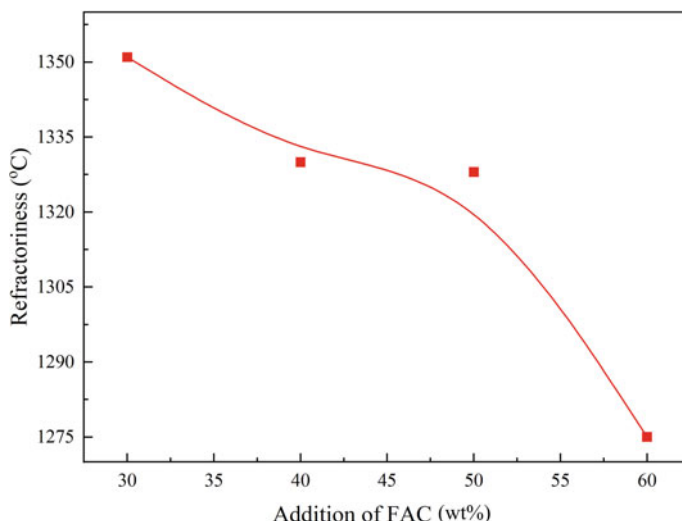


Fig. 5.57 Effect of FAC addition on the refractoriness of the sample

5.4.2 Effect of Sintering Temperature

The effect of sintering temperature on the bulk density, apparent porosity, compressive strength, thermal conductivity, and refractoriness of the sample was studied by fixing the magnesite addition of 15 wt%, FAC addition of 50 wt%, and sintering time of 3 h. As shown in Fig. 5.58, as the sintering temperature increased from 900 °C to 1200 °C, the bulk density of the sample increased from 0.95 g/cm³ to 1.35 g/cm³, with the decrease of apparent porosity from 36.38% to 31.97%. Meanwhile, the compressive strength increased from 0.7 MPa to 17.07 MPa. However, when the sintering temperature increased from 900 °C to 1200 °C, the thermal conductivity and refractoriness of the sample changed slightly (Figs. 5.59 and 5.60). The recommended sintering temperature was 1100 °C.

5.4.3 Effect of Sintering Time

The effect of sintering time on the bulk density, apparent porosity, compressive strength, thermal conductivity, and refractoriness of the sample was studied by fixing the magnesite addition of 15 wt%, FAC addition of 50 wt%, and sintering temperature of 1100 °C. As shown in Fig. 5.61, when the sintering time increased, the bulk density and compressive strength of the sample increased gradually and the apparent porosity decreased gradually. As shown in Fig. 5.62, with the extension of sintering time, the thermal conductivity of the sample increased. As shown in Fig. 5.63, when

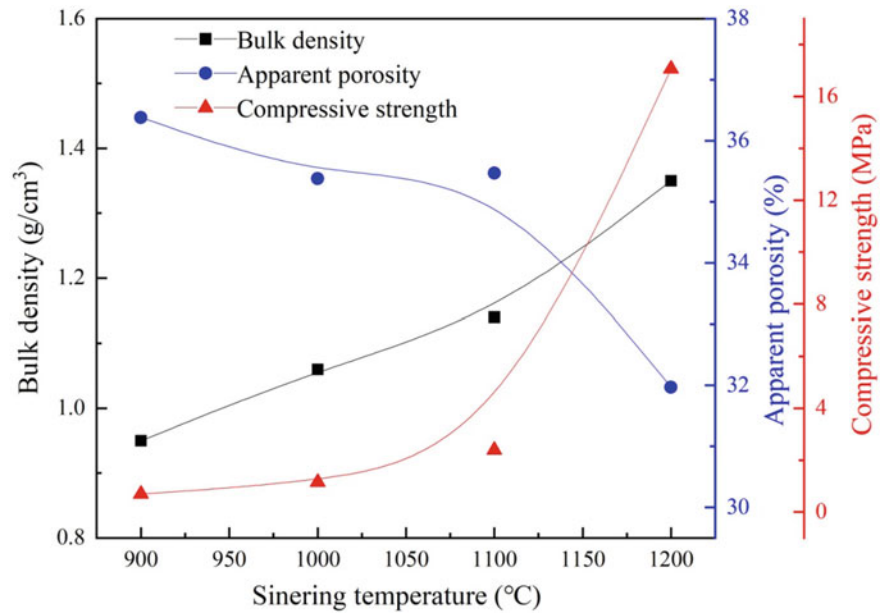


Fig. 5.58 Effects of sintering temperature on the bulk density, apparent porosity, and compressive strength of the sample

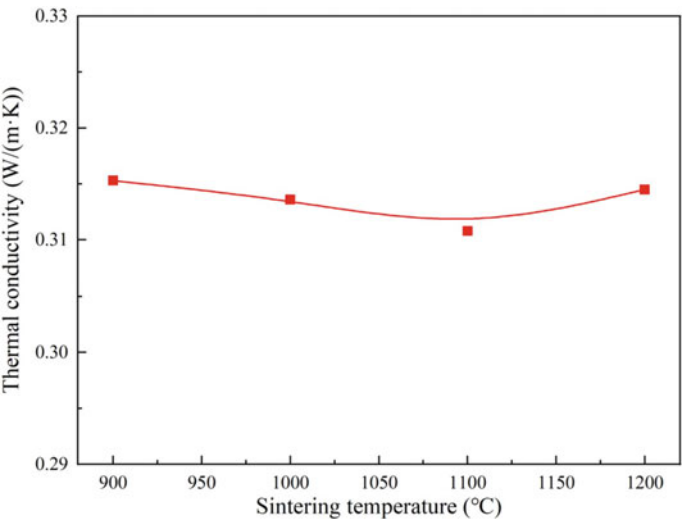


Fig. 5.59 Effect of sintering temperature on the thermal conductivity of the sample

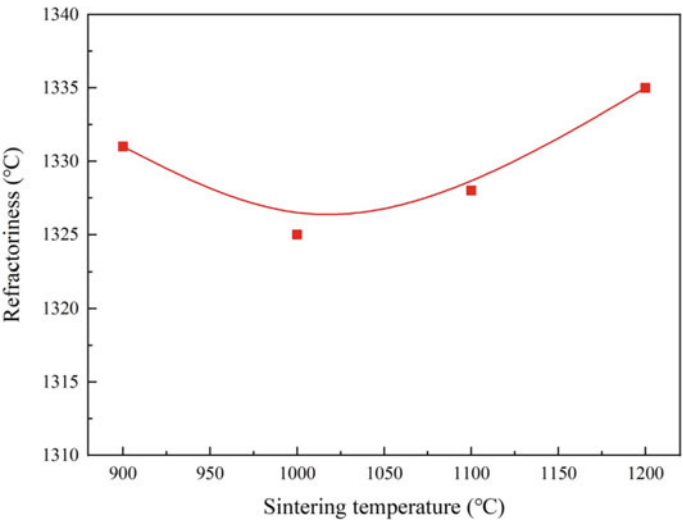


Fig. 5.60 Effect of sintering temperature on the refractoriness of the sample

the sintering time changed from 1 to 4 h, the refractoriness of the sample changed slightly. Obviously, the suitable sintering time was 3 h.

The above results showed that a good lightweight thermal insulation material with bulk density of 1.14 g/cm³, apparent porosity of 35.47%, compressive strength of 2.39 MPa, thermal conductivity of 0.3108 W/(m·K) and refractoriness of 1328 °C could be obtained under the conditions of magnesite addition of 15 wt%, FAC addition of 50 wt%, sintering temperature of 1100 °C, and sintering time of 3 h.

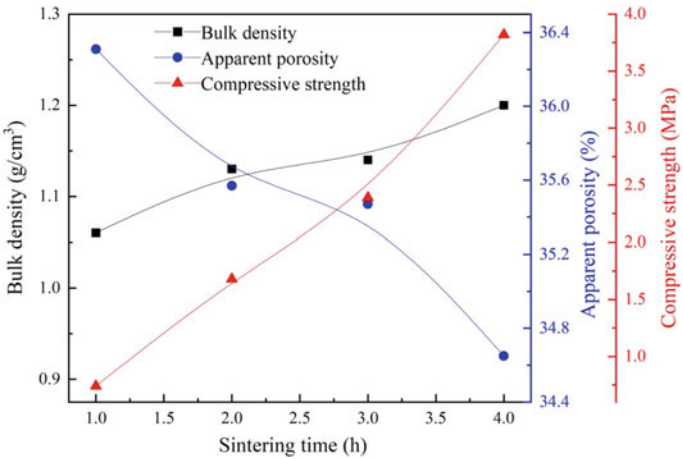


Fig. 5.61 Effects of sintering time on the bulk density, apparent porosity, and compressive strength of the sample

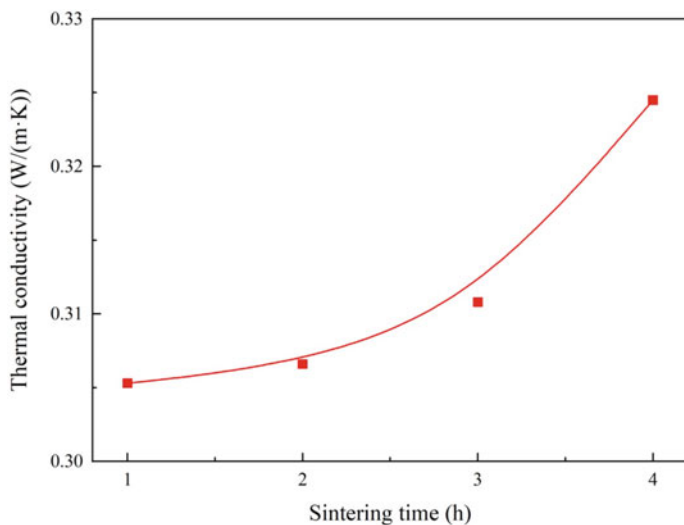


Fig. 5.62 Effect of sintering time on the thermal conductivity of the sample

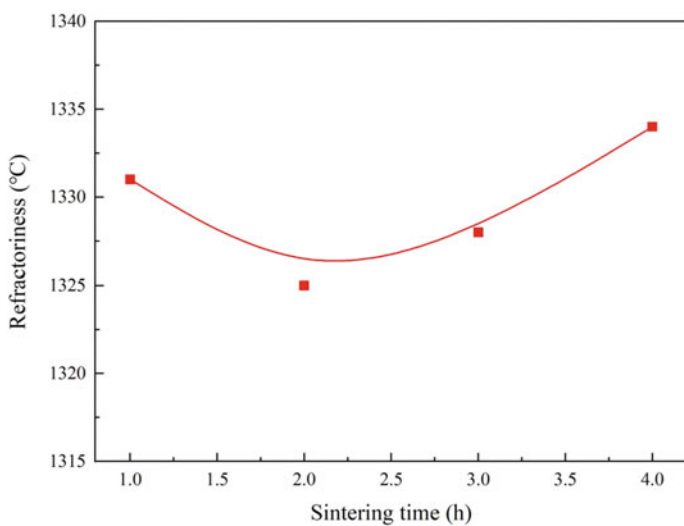


Fig. 5.63 Effect of sintering time on the refractoriness of the sample

It is concluded that preparing forsterite refractory materials and lightweight thermal insulation materials from ferronickel slag has good raw material compatibility, high process controllability, great flexibility, low cost, and high added value.

Overall, the new methods for preparation of refractory materials and thermal insulation materials using ferronickel slag were developed based on the characteristics of chemical composition and phase composition of the slag. Their advantages, such as low raw material cost, high product added value, and environmental friendliness, make them have good application prospects, deserving further research.

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Chapter 6

Recycling of Stainless-Steel Pickling Sludge via RKEF Route



Abstract Stainless-steel pickling sludge (SSPS) is a hazardous solid waste, mainly containing CaSO_4 , CaF_2 and certain amounts of Fe, Cr and Ni. The abundant sulfur in the SSPS hinders its utilization and deteriorates the product quality when the sludge is recycled as the feed for ferronickel production. In this chapter, we introduce a method of coprocessing of SSPS and laterite ore via the rotary kiln-electric furnace (RKEF) process. The desulfurization behaviors of SSPS, including the thermodynamics, phase transformation and off-gas emission characteristics during reductive roasting were primarily investigated. The presence of laterite ore enhanced the desulfurization of SSPS which could facilitate the subsequent reductive smelting of the calcine obtained by reductive roasting.

Keyword Stainless-steel pickling sludge · Desulfurization · Recycling · Calcium sulfate · RKEF process

Stainless steel is widely used and its output in China was 30.63 million tons in 2021, ranking first in the world. Stainless-steel strips need surface pickling to improve their corrosion resistance and appearance using acids, such as H_2SO_4 , HNO_3 and HF [1, 2]. Consequently, stainless-steel pickling sludge (SSPS), which contains calcium sulfate, calcium fluoride and a significant amount of Cr and Ni [3, 4], is generated from neutralization and precipitation of pickling acidic wastewater. It is a hazardous waste, threatening human health and the environment [5].

The discharge of SSPS is about 30–50 kg/per ton of stainless-steel [6]. For treatment of SSPS, the landfill disposal after solidification/stabilization has a relatively low cost [7, 8], but the problem of secondary environmental pollution may still exist. The hydrometallurgical processes are performed to recycle valuable metals by acid leaching, and leaching of iron, nickel and chromium could exceed 99.8%, 99.3% and 99.2%, respectively [9]. Nevertheless, the hydrometallurgical process faces issues of large emission of wastewater and secondary solid waste.

Pyrometallurgical processes such as reductive smelting and direct reduction are preferential because of their simple process flow and high efficiency [10–13]. The rotary kiln-electric furnace (RKEF) process is one of the most efficient ferronickel production technologic routes. The feed is usually pre-reduced in a rotary kiln at 800–950 °C followed by reductive smelting at 1500–1550 °C in an electric furnace for

Table 6.1 Chemical composition of dried SSPS (wt%)

Element	F	Na	S	Cl	K	Ca	Fe	Ni	Cr	C	O
Content	5.77	0.06	9.10	0.03	0.05	21.66	10.31	0.28	2.85	1.28	48.1

separation of alloy from slag. In view of this fact, for current ferronickel production plants, the RKEF process can be adopted to recycle valuable metals from SSPS. Nevertheless, due to the presence of excessive sulfur in the SSPS which will enter into steel after reductive smelting [14], it is crucial to have desulfurization in the pre-reduction stage for environmentally friendly and high-efficiency utilization of SSPS.

In light of the enhanced desulfurization of CaSO_4 by Fe_2O_3 , SiO_2 or Al_2O_3 , which could be provided by laterite ore, the concept of coprocessing of SSPS and laterite ore in the RKEF process was put forward and validated. As desulfurization is essential to the utilization of SSPS by the RKEF process, the desulfurization behaviors of SSPS including the reaction thermodynamics, phase transformation and off-gas emission characteristics during reductive roasting (also known as pre-reduction) were investigated. Furthermore, reductive smelting of the roasting product, calcine, was conducted for metal recovery [15].

6.1 Properties of SSPS

The SSPS sample was obtained from a plant in China. Its moisture content was 50%. It was firstly dried at 105 °C for 3 h to remove its free water and then ground to particles with size less than 150 μm . The chemical composition of SSPS is shown in Table 6.1. The sulfur content was 9.1 wt% and the corresponding CaSO_4 content would be 38.7 wt% by assuming that sulfur solely existed in the form of CaSO_4 .

The XRD pattern and morphology of dried SSPS is shown in Fig. 6.1. The main phases of dried SSPS were gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), calcium fluoride (CaF_2) and calcium carbonate (CaCO_3). The Fe, Ni, Cr-bearing phases were not observed because of poor crystallization of their hydroxides. Additionally, the nickel content in SSPS was too low to be detected. The morphology of SSPS particles was irregular.

6.2 Desulfurization During Reductive Roasting of SSPS with Laterite Ore

The used laterite ore was firstly dried at 105 °C for 3 h and then ground to particles with size less than 150 μm . The chemical composition of laterite ore is shown in

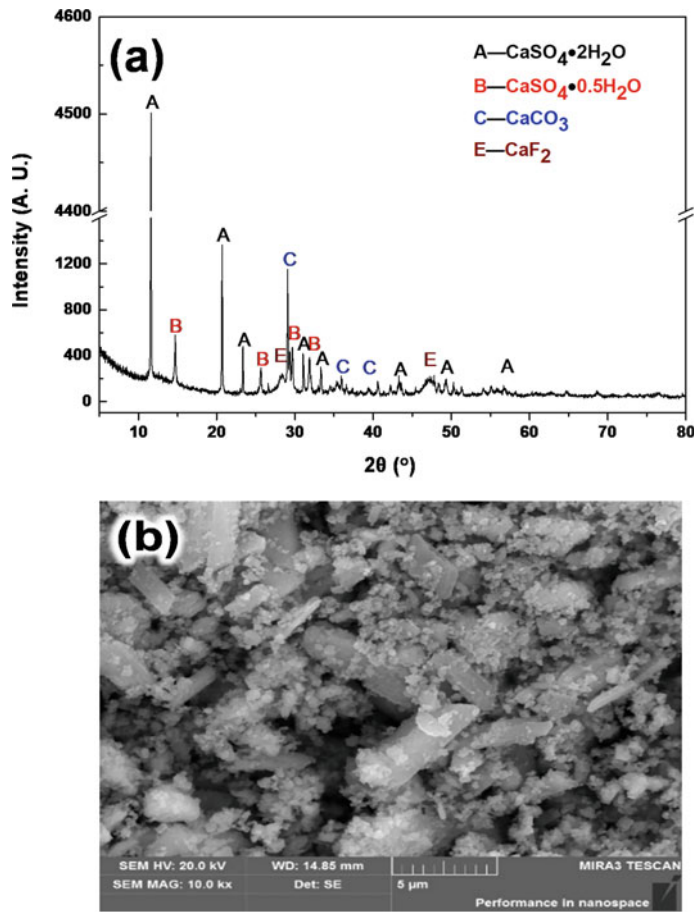


Fig. 6.1 XRD pattern and morphology of dried SSPS

Table 6.2. The contents of Fe₂O₃, SiO₂ and MgO were 31.6%, 26.5% and 13.4%, respectively. The main phases of laterite ore were lizardite ((Mg, Al)₃(Si, Fe)₂O₄(OH)₄), goethite (FeO(OH)), hematite (Fe₂O₃) and quartz (SiO₂).

Coke breeze with particle size less than 150 μm was used as the reductant. Its proximate and ultimate analysis is shown in Table 6.3.

Table 6.2 Main chemical composition of laterite ore (wt%)

Component	Ni	Fe ₂ O ₃	SiO ₂	MgO	Al ₂ O ₃	CaO	Cr ₂ O ₃	S	LOI*
Content	1.9	31.6	26.5	13.4	4.3	2.0	1.7	0.05	13.2

*LOI—loss on ignition

Table 6.3 Proximate and ultimate analyses of coke breeze (wt%)

Proximate analysis				Ultimate analysis				
Moisture content	Ash content	Volatile matter content	Fixed carbon content	C	H	O	N	S
0.51	13.12	1.77	84.60	86.6	0.44	0.95	0.87	0.75

The dried SSPS was firstly mixed with laterite ore and/or coke breeze and then the mixture was pelletized into green pellets with diameters in the range of 10–12 mm. The green pellets were dried at 105 °C for 3 h in an oven. Reductive roasting was carried out in a horizontal tube furnace and the roasting temperature was controlled by a K-type thermocouple. High-purity N₂ gas with a flow rate of 2 L/min was flushed into the tube to exhaust air. When the temperature reached the target temperature, the dried pellets loaded in a corundum crucible were pushed into the furnace for roasting.

After roasting, the pellets were cooled, crushed and ground to obtain powdered calcine, which was mixed with a certain amount of coke breeze (5 wt%) and then charged into a corundum crucible in a furnace for reductive smelting. During the whole procedure, high-purity N₂ gas was used to flush the air and the smelting temperature was kept at 1450 °C for 60 min.

The chemical compositions of the samples were analyzed by the methods including ion selective electrode method for determining contents of F and Cl (ISE, Leici, China), high-frequency infrared carbon–sulfur analyzer for determining contents of C and S (CS-3000 Beijing Nake, China), and atomic absorption spectroscopy for determining contents of Ni, Fe, Cr, Ca, etc. (AAS, PinAAcle 900 T PerkinElmer, USA). The desulfurization degree of SSPS was calculated as follows:

$$\gamma = \frac{(M_1 \times \alpha - M_2 \times \beta)}{M_1 \times \alpha} \times 100\% \quad (6.1)$$

where γ is desulfurization degree; M_1 is the mass of the sample before roasting; M_2 is the mass of calcine; α is the sulfur content of sample before roasting and β is the sulfur content of calcine.

6.2.1 Effect of Coke Breeze and SSPS Additions

By fixing the reductive roasting temperature of 900 °C and roasting time of 60 min, the variations of desulfurization degree of SSPS with coke breeze and SSPS additions are shown in Fig. 6.2. Coke breeze played an important role in the desulfurization. The desulfurization degree increased significantly from 33.05% to 91.52% with the addition of 1.5 wt% coke breeze. However, when the coke breeze addition was higher than 3 wt%, the desulfurization degree and sulfur content in the calcine kept

almost constant. The desulfurization degree decreased with increasing addition of SSPS in the absence of coke breeze, while it increased in the presence of 3 wt% coke breeze as the amount of CaSO_4 increased with the SSPS addition.

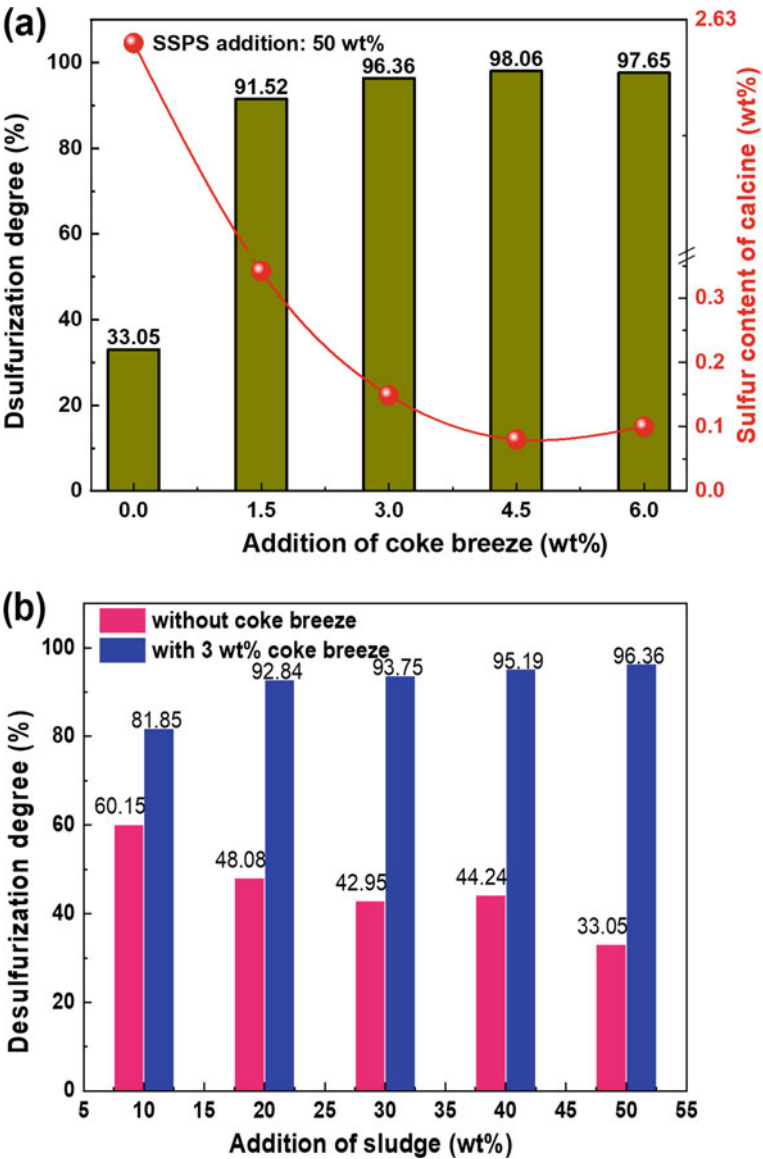


Fig. 6.2 Variations of desulfurization degree of SSPS with **a** coke breeze addition and **b** SSPS addition by fixing roasting temperature of 900 °C and roasting time of 60 min

6.2.2 Effect of Reductive Roasting Temperature and Time

By fixing the SSPS and coke breeze additions at 50 wt% and 4.5 wt%, respectively, the variations of desulfurization degree of SSPS with roasting temperature and time are shown in Fig. 6.3.

The reductive roasting temperature was crucial to the desulfurization of SSPS. As the temperature increased from 700 °C to 850 °C, the desulfurization degree

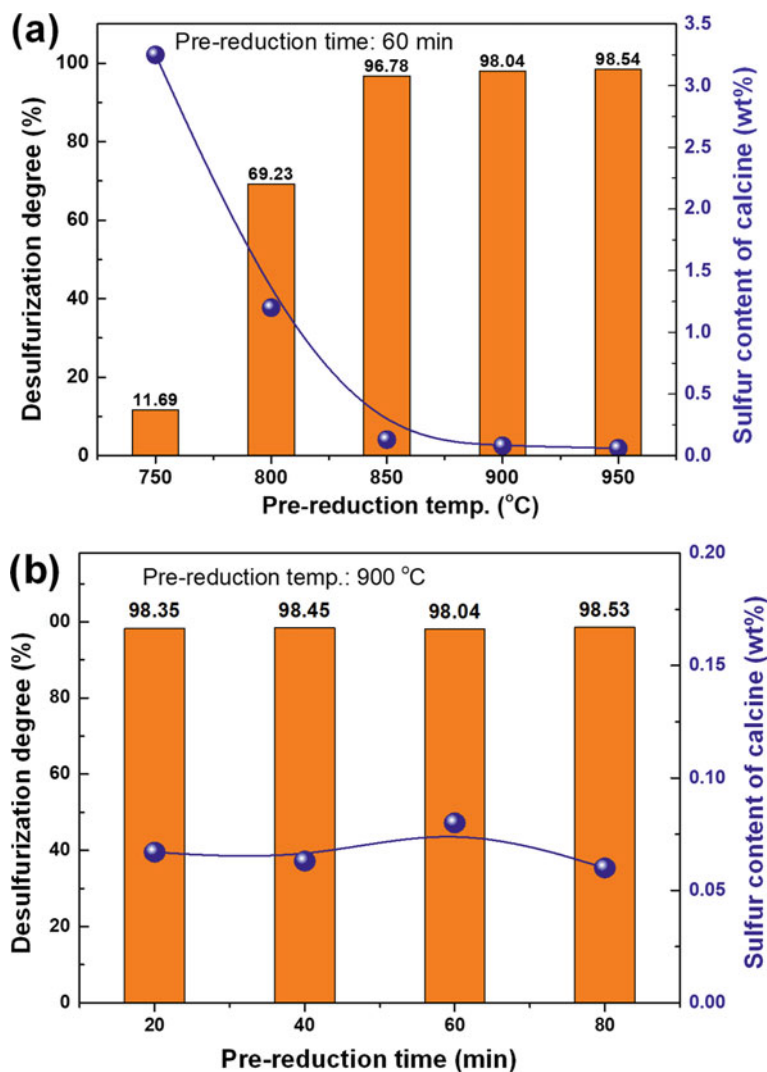


Fig. 6.3 Variations of desulfurization degree of SSPS with **a** roasting temperature and **b** roasting time by fixing SSPS addition of 50 wt% and coke breeze addition of 4.5 wt%

sharply increased from 11.69% to 96.78% and the sulfur content in the calcine decreased from 3.25 wt% to 0.13 wt%. Nevertheless, the desulfurization degree kept nearly constant as the roasting temperature exceeded 850 °C. This was mainly because the main sulfur-containing phase, CaSO_4 , in SSPS hardly decomposed at low temperatures, whereas CaSO_4 would react with the components from laterite ore to discharge SO_2 at high temperatures. Thus, the proper reductive roasting temperature for desulfurization of SSPS should be higher than 850 °C for sufficient sulfur removal. By contrast, the influence of roasting time was relatively small as the desulfurization degree readily exceeded 98% after reduction for 20 min. It proved that the CaSO_4 in SSPS would quickly decompose to SO_2 during co-roasting of SSPS and laterite ore at 900 °C.

6.2.3 Mechanisms of Desulfurization

The phase transformation and SO_2 emission characteristics during roasting as well as the related reaction thermodynamics were investigated to shed a light on the desulfurization mechanisms. The XRD patterns of the calcines obtained by reductive roasting of SSPS and laterite ore under different conditions are shown in Figs. 6.4 and 6.5.

In general, CaSO_4 is difficult to decompose in an oxidative atmosphere or inert atmosphere. However, the presence of reducing agent can lower the decomposition temperature of CaSO_4 . However, the products of decomposition of CaSO_4 may be CaO or CaS , which are dependent on the reduction temperature and the reduction potential (molar ratio of CO to CO_2) [16], while the formation of CaS is unfavorable for the desulfurization of CaSO_4 . It has been reported that CaSO_4 tended to convert into CaO at a low reduction potential and the proper temperature for the sulfur removal from the pickling sludge was 800–1000 °C [17]. Moreover, the additives such as Fe_2O_3 , SiO_2 , Al_2O_3 were found to be able to promote the desulfurization of CaSO_4 and impede the formation of CaS [18, 19].

The CaSO_4 remained in the calcine explained the low desulfurization degree (only 48.08%), as shown in Fig. 6.3b, while it disappeared with increasing addition of coke breeze. Additionally, as the SSPS addition increased from 20 wt% to 50 wt%, diopside ($\text{CaMgSi}_2\text{O}_6$) was formed.

As for the effect of reduction temperature (Fig. 6.5b), MgSiO_3 which was derived from the decomposition of lizardite and CaSO_4 in the calcine obtained at 750 °C. As the temperature exceeded 800 °C, the phase of MgSiO_3 disappeared with the formation of $\text{CaMgSi}_2\text{O}_6$. Thus, it was proposed that SiO_2 and MgSiO_3 from laterite ore would react with CaSO_4 in SSPS, promoting the desulfurization of SSPS.

According to the phase transformation during roasting, possible reactions and their Gibbs free energy changes that lead to the desulfurization of CaSO_4 are listed and plotted in Table 6.4 and Fig. 6.6, respectively. The reduction reactions of CaSO_4 by CO with the formations of different products CaO and CaS are given by Eq. 6.2

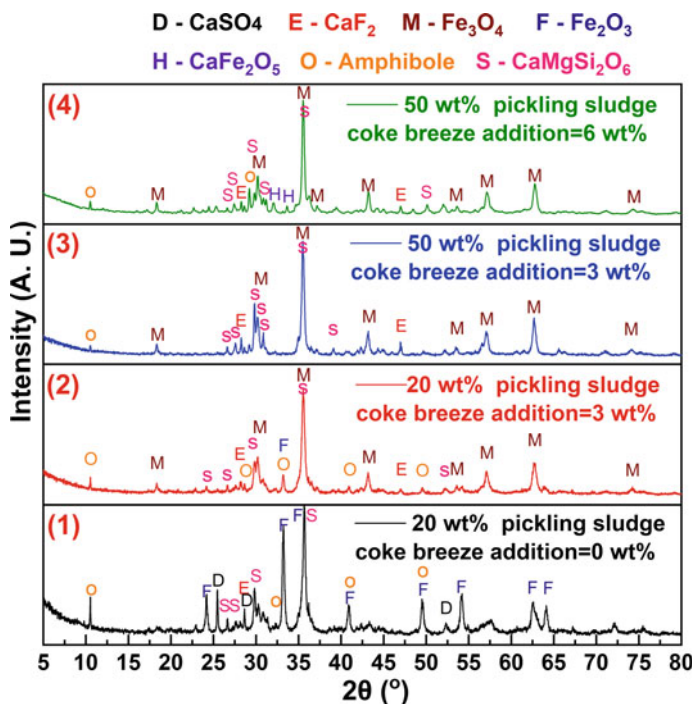


Fig. 6.4 XRD patterns of the calcines obtained after roasting with different additions of SSPS and coke breeze by fixing roasting temperature of 900 °C and roasting time of 60 min

and Eq. 6.3, respectively. In the presence of SiO₂ and MgO (or MgSiO₃) which were derived from laterite ore, the reactions for the decomposition of CaSO₄ with the formation of CaMgSi₂O₆ are expressed by Eqs. 6.4 to 6.7.

As shown in Fig. 6.7, although CaSO₄ was readily reduced to CaS at low temperatures, the presence of MgO, MgSiO₃ and SiO₂ would react with CaSO₄ to promote the generation of SO₂ other than CaS under reducing atmosphere. It was also obvious that the formation of CaS was inhibited with decreasing partial pressure of SO₂ from 1 atm to 0.01 atm as the reductive roasting temperature exceeded 900 °C. As high-purity nitrogen gas was flushed with a flow rate of 2 L/min, the partial pressures of SO₂ and O₂ were lower than 0.01 atm. Therefore, Eqs. 6.6 and 6.7 would be preferential to Eq. 6.3, facilitating the removal of sulfur.

According to the SO₂ emission characteristics shown in Fig. 6.6, both the roasting temperature and carbon content played important roles in the desulfurization of SSPS. Almost no SO₂ was detected from the off-gas during roasting without the addition of coke breeze. When the temperature was higher than 800 °C, CaSO₄ decomposed to release SO₂. On the other hand, increasing temperature accelerated the desulfurization progress, as proved by the shortened SO₂ emission interval.

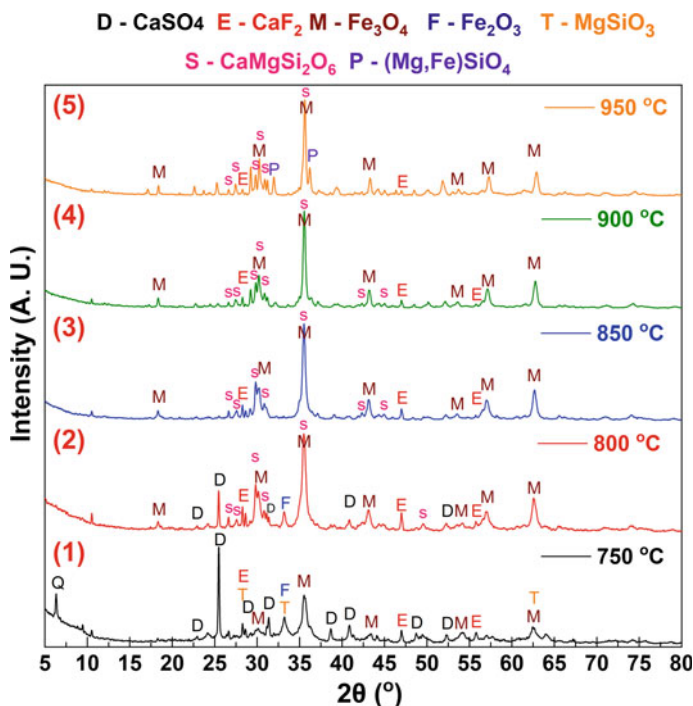


Fig. 6.5 XRD patterns of the calcines obtained after roasting at different temperatures by fixing SSPS addition of 50 wt% and roasting time of 60 min

Table 6.4 Possible reactions concerning the decomposition of CaSO₄ in the presence of laterite ore

Reaction	Equation
$\text{CaSO}_4 + \text{CO} = \text{CaO} + \text{SO}_2 + \text{CO}_2$	6.2
$\text{CaSO}_4 + 4\text{CO} = \text{CaS} + 4\text{CO}_2$	6.3
$\text{CaSO}_4 + \text{SiO}_2 + \text{MgSiO}_3 = \text{CaMgSi}_2\text{O}_6 + \text{SO}_2 + \frac{1}{2}\text{O}_2$	6.4
$\text{CaSO}_4 + 2\text{SiO}_2 + \text{MgO} = \text{CaMgSi}_2\text{O}_6 + \text{SO}_2 + \frac{1}{2}\text{O}_2$	6.5
$\text{CaSO}_4 + \text{SiO}_2 + \text{MgSiO}_3 + \text{CO} = \text{CaMgSi}_2\text{O}_6 + \text{SO}_2 + \text{CO}_2$	6.6
$\text{CaSO}_4 + 2\text{SiO}_2 + \text{MgO} + \text{CO} = \text{CaMgSi}_2\text{O}_6 + \text{SO}_2 + \text{CO}_2$	6.7

6.3 Smelting of Calcine for Metal Recovery

After reductive roasting, the calcines obtained were subjected to reductive smelting and the metal recoveries from two calcines (with and without the addition of SSPS)

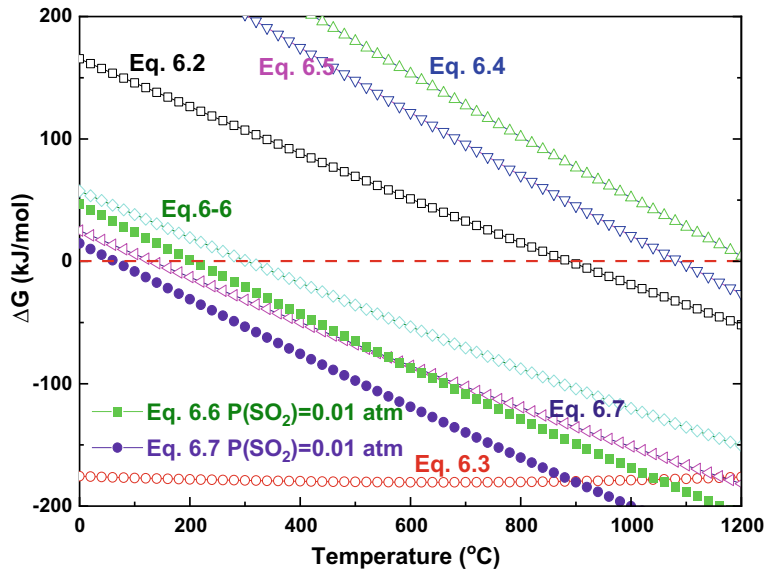


Fig. 6.6 Plots of standard Gibbs free energy changes of possible reactions against temperature (solid shapes representing SO₂ partial pressure of 0.01 atm)

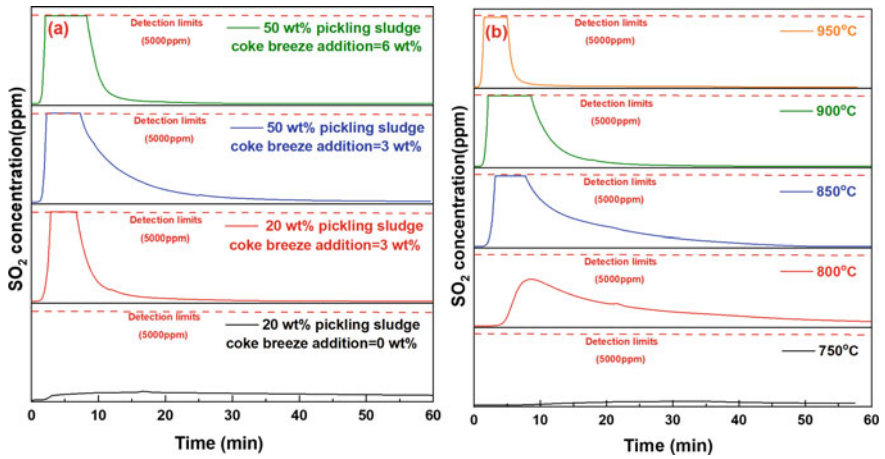


Fig. 6.7 Variations of SO₂ concentration with **a** SSPS and coke breeze additions at 900 °C for 60 min and **b** roasting temperature by fixing SSPS addition of 50 wt%, coke breeze addition of 4.5 wt%, and reduction time of 60 min. Reprinted from ref. [15], copyright 2022, with permission from Elsevier

were taken into account for comparison. The chemical compositions of the calcines are shown in Table 6.5. The contents of different iron species (i.e. Fe_{total} , FeO and $\text{Fe}_{\text{metallic}}$) were determined by chemical titration as described in our previous report [20].

As shown in Fig. 6.8, the presence of SSPS improved the recovery of metals, especially Fe and Ni, rising from 69.05% to 97.72% and 60.4% to 81.9%, respectively. It was attributed to the fact that the residual CaO derived from the decomposition of CaSO_4 increased the slag basicity and decreased the viscosity of slag associated with the formation of diopside with low melting point. Besides, CaF_2 from SSPS would also improve the separation during smelting.

The calcine in the presence of SSPS had better separation after smelting than that without the addition of SSPS. The main phase components of the slag solely from smelting of laterite ore were MgSiO_3 and Fe , while diopside ($\text{CaMgSi}_2\text{O}_6$) and fluorocannilloite ($\text{Ca}_3\text{Mg}_4\text{AlSi}_5\text{Al}_3\text{O}_{22}\text{F}_2$) were formed in the slag by adding 50 wt% SSPS. The SEM–EDS results of these two slags further verified the improvement

Table 6.5 Chemical compositions of the calcines obtained by reductive roasting at 900 °C for 40 min with coke breeze addition of 4.5 wt%

Feed	Chemical composition (wt%)						Reduction degree of iron oxides
	Fe_{total}	FeO	$\text{Fe}_{\text{metallic}}$	Ni	Cr	S	
Laterite ore with the addition of 50 wt% SSPS	24.81	3.86	1.87	1.88	1.67	0.125	11.2
Laterite ore	26.44	2.98	0.92	2.27	1.00	0.09	6.4

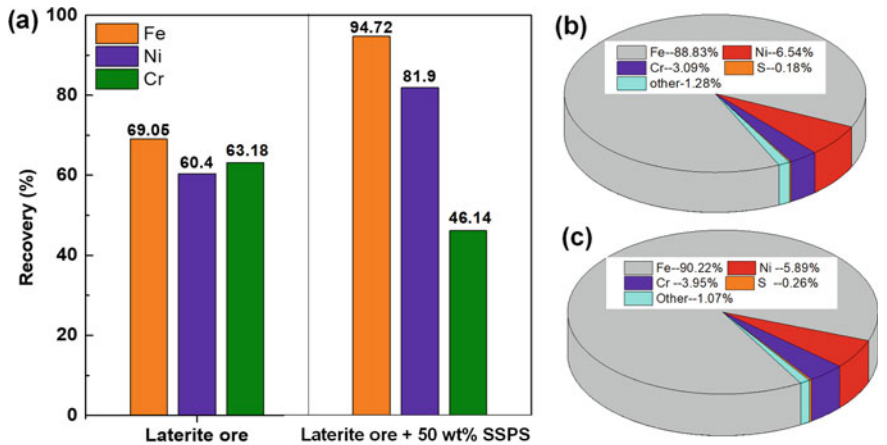


Fig. 6.8 a Metals recoveries in the smelting procedure and chemical compositions of the obtained alloys after smelting of b laterite ore, and c laterite ore with the addition of 50 wt% SSPS. Reprinted from ref. [15], copyright 2022, with permission from Elsevier

of smelting performance by adding SSPS. Thus, one could conclude that coprocessing of SSPS and laterite ore can eliminate the hazards of SSPS with simultaneous recycling of metals, e.g., iron, nickel and chromium, by adopting the RKEF route.

During reductive roasting, roasting temperature and reductant were crucial for desulfurization of SSPS and the reduction temperature should be higher than 850 °C for sufficient sulfur removal. The components like MgO and SiO₂ from laterite ore enhanced the desulfurization of SSPS by forming CaMgSi₂O₆ and SO₂. After reductive roasting at 900 °C for 40 min, the desulfurization degree approached 98.35% and the sulfur content of the calcine was 0.06 wt% from the mixture of laterite ore, 50 wt% SSPS and 4.5 wt% coke breeze. Moreover, the SO₂ in the flue gas could be removed by the widely used flue gas desulfurization (FGD) process.

In the reductive smelting stage, the residual CaO and CaF₂ from SSPS served as fluxes for slag forming. Thus, the presence of SSPS was favorable for reductive smelting and the recoveries of Fe, Ni and Cr were 94.72%, 81.90% and 46.14%, respectively.

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