Rare Metal Materials and Engineering
Volume 54, Issue 5, May 2025
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Guo Peimin, Shen Yaozong, Wang Lei, et al. Theory and Method of Transformative Metallurgy (Dissociation and Purification) of Beryllium Ore[J]. Rare Metal Materials and Engineering, 2025, 54(05): 1207-1216. DOI: https://doi.org/10.12442/j.issn.1002-185X.20240130.

ARTICLE

Theory and Method of Transformative Metallurgy (Dissociation and Purification) of Beryllium Ore

Guo Peimin1,2, **Shen Yaozong**1,2, **Wang Lei**1,2, **Kong Lingbing**1,2, **Wang Dongxin**4, **Guo Qing**3

1 State Key Laboratory for Advanced Iron and Steel Processes and Products, Central Iron and Steel Research Institute Co., Ltd, Beijing 100081, China; 2 CISRI Sunward Technology Co., Ltd, Beijing 100081, China; 3 China Minmetals Beryllium Co., Ltd, Hengyang 421513, China; 4 Northwest Rare Metal Material Research Institute Ningxia Co., Ltd, Shizuishan 753000, China

Abstract: A transformative beryllium metallurgy theory and method was proposed based on the low-temperature dissociation of hydrofluoric acid and purification by exploiting the large difference of fluoride solubility. Hydrofluoric acid can quickly dissociate beryllium ore powder directly at low or room temperature with more than 99% dissociation rate. The solubility of AlF_3, FeF_3, CrF_3, and MgF_2 is low. Coupled with common ion effect, 99.9%-purity beryllium products can be prepared without chemical purification. For high-purity beryllium products of grade 4N or higher, they can be prepared through the superior property that the pH intervals of iron, chromium, and other hydroxide precipitates are distinctly different from those corresponding to $Be(OH)_2$ precipitates. This new method can be used to prepare most of the beryllium products that are prepared by modern beryllium metallurgy.

Key words: beryllium ore metallurgy; sulfuric acid; hydrofluoric acid; purity; yielding rate; environmental protection

1 Introduction

Beryllium is the known lightest metal structural material with high strength[1–4], high modulus of elasticity, low density, small coefficient of thermal expansion, good thermal shock resistance, and fine thermal diffusivity[5–8], which is an important strategic resource in aerospace and nuclear industries[9–14].

The electric furnace-leaking with sulfuric acid is the current main method for beryllium ore dissociation[15–17], which destroys the structure of beryllium ore under high temperature conditions, then dissociates it with sulfuric acid to obtain beryllium-containing solution, and subsequently purifies it by extraction method and chemical precipitation to obtain BeO with purity of 98%–99%. Finally, various beryllium products, such as BeO ceramics, beryllium-copper alloys, BeF_2, and metallic beryllium beads, can be prepared from BeO[18–22].

With the increasingly strict requirements on environmental protection[23–26], the abovementioned methods are restricted to a certain extent because they may cause serious environmental risks. In the extraction process of beryllium, the slag is an incremental process, and for every ton of beryllium ore processed, the amount of slag will be increased by more than ten times accordingly. The generated silicon slag and alumina slag containing 0.5%–1.5% BeO are hazardous wastes, which are not easy to treat and have great environmental risks. The large amount of hazardous waste slag and the large quantities of BeO contained in the slag jointly result in the yielding rate of only 75% of beryllium in the process of preparing BeO from beryllium ore. In the process of beryllium metal preparation, the direct yielding rate of beryllium in $(NH_4)_2BeF_4$ thermal decomposition, beryllium bead magnesium thermal reduction, and beryllium copper alloy preparation processes is less than 30%, and the comprehensive yielding rate is less than 50%, which results in a serious waste of beryllium resources. In addition, due to the lack of high-purity beryllium, the purity and various properties of high-end beryllium products are affected, and advanced technology is required to further improve the purity of beryllium.

Received date: June 08, 2024
Foundation item: National Key Research and Development Program of China (2021YFC2902301, 2021YFC2902302)

Corresponding author: Guo Peimin, Ph. D., Professor, State Key Laboratory for Advanced Iron and Steel Processes and Products, Central Iron and Steel Research Institute Co., Ltd, Beijing 100081, P. R. China, E-mail: guopm@pku.org.cn

Based on the abovementioned technical difficulties, the Ministry of Science and Technology of the People's Republic of China has set up a key research and development project: *Beryllium Green metallurgy and Deep Processing*. The project focuses on the research of the theory and method of transformative metallurgy of beryllium ore. In this research, the differences between traditional beryllium ore metallurgy and transformative metallurgy theories and the methods to provide new theories for the green and efficient preparation of high-purity beryllium products were investigated.

2 Changes in Theory of Beryllium Metallurgy (Dissociation and Purification)

2.1 Modern beryllium metallurgy theory

2.1.1 Destruction of beryllium mineral phase by high temperature melting

The ore for beryllium metallurgy is mainly beryl ore, whose main structure is $3BeO\cdot Al_2O_3\cdot 6SiO_2$. The structure of beryl is a hexagonal system with a_0=0.9188 nm, c_0=0.9189 nm, and coordination number Z=2, and this structure is stable. Due to the direct leaching of beryllium ore with sulfuric acid, the dissociation rate is low. Therefore, before leaching with sulfuric acid, calcination in an electric furnace was required to dissociate the beryl phase of beryllium ore into easily dissociable $CaO\cdot 3BeO\cdot 2SiO_2$ using calcite, and the high temperature reactions are shown in Eq.(1–2), as follows:

$$3BeO\cdot Al_2O_3\cdot 6SiO_2 + 2CaCO_3 = CaO\cdot Al_2O_3\cdot 2SiO_2 + CaO\cdot 3BeO\cdot 2SiO_2 + 2SiO_2 + 2CO_2 \quad (1)$$

$$3BeO\cdot Al_2O_3\cdot 6SiO_2 + 4CaCO_3 = CaO\cdot Al_2O_3\cdot 2SiO_2 + CaO\cdot 3BeO\cdot 2SiO_2 + 2CaO\cdot SiO_2 + 4CO_2 \quad (2)$$

The modified oxide slag obtained from high temperature melting was quenched by water and turned into beryllium vitreous. Subsequently, the lumpy glass slag was turned into fine powder by ball milling and then put into the sulfuric acid leaching reactor.

2.1.2 Sulfuric acid leaching

Various oxides in beryllium glass slag can react with sulfuric acid, and the reactions are shown in Eq.(3–7), as follows:

$$CaO\cdot 3BeO\cdot 2SiO_2 + 4H_2SO_4 = CaSO_4 + 3BeSO_4 + 2H_2SiO_3 + 2H_2O \quad (3)$$

$$CaO\cdot Al_2O_3\cdot 2SiO_2 + 4H_2SO_4 = CaSO_4 + Al_2(SO_4)_3 + 2H_2SiO_3 + 2H_2O \quad (4)$$

$$CaO\cdot SiO_2+H_2SO_4=CaSO_4+H_2SiO_3 \quad (5)$$

$$Fe_2O_3+3H_2SO_4=Fe_2(SO_4)+3H_2O \quad (6)$$

$$Cr_2O_3+H_2SO_4=Cr_2(SO_4)_3+3H_2O \quad (7)$$

2.1.3 pH chemical separation

$CaSiO_3$ and $CaSO_4$ are the products of sulfuric acid leaching, they show slight solubility, and most of them are obtained as silicon residue by liquid-solid separation. $BeSO_4$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$, and other sulfates are soluble, and their solubility is listed in Table 1[27–30]. According to Table 1, it is impossible to separate $BeSO_4$ from other soluble sulfates directly by solubility.

Table 1 Solubility of different sulfates in water at 25 °C[27–30]

Sulfate	Solubility in aqueous solution/g·(100 g)$^{-1}$
$BeSO_4$	39.1
$Al_2(SO_4)_3$	36.4
$Fe_2(SO_4)_3$	440
$Cr_2(SO_4)_3$	220
$CaSO_4$	0.255
$MgSO_4$	33.7

The use of pH adjustment for stepwise precipitation centers on the fact that it is important to distinguish the pH range of $Be(OH)_2$ precipitation from the pH range of several other hydroxide precipitates. As shown in Fig.1, the pH ranges for Al^{3+}, Cr^{3+}, and Be^{2+} precipitation highly overlap, which cannot be applied to pH precipitation separation. The pH ranges for Fe^{3+} and Be^{2+} partially overlap, which can be used in the chemical precipitation method to remove part of the iron, but this method may result in the existence of Be^{2+} in the product. Due to the high concentration of aluminum in the solution, it is necessary to remove Al^{3+} by other chemical methods, and then to remove Fe^{3+} by the pH precipitation method.

2.1.4 $NH_4Al(SO_4)_2$ precipitation removal of Al^{3+}

$(NH_4)_2SO_4$ can react with $Al_2(SO_4)_3$ to form $NH_4Al(SO_4)_2$ and the reaction is shown in Eq.(8), as follows:

$$(NH_4)_2SO_4+Al_2(SO_4)_3=2NH_4Al(SO_4)_2 \quad (8)$$

The saturated solubility of $NH_4Al(SO_4)_2$ varies greatly with temperature. The saturated solubility of $NH_4Al(SO_4)_2$ in the room temperature state is as low as only 5–7 g·(100 g)$^{-1}$, and it can be more than 100 g·(100 g)$^{-1}$ at 110 °C. The solubility of Al^{3+} and Be^{2+} is shown in Fig. 2, and the solubility of $NH_4Al(SO_4)_2$ can be controlled to 1–1.5 g·(100 g)$^{-1}$ at room temperature (25–30 °C) under a certain $NH_4Al(SO_4)_2$ concentration. The molar concentration ratio of Al^{3+} and Be^{2+} under this condition is $Al^{3+}/Be^{2+}<0.025$, which can satisfy the requirement for BeO (purity of 98%) product preparation.

2.1.5 Preparation of metal beryllium

To prepare beryllium metal, $Be(OH)_2$ was converted to BeF_2, and then beryllium metal beads were prepared by thermal reduction with magnesium. The raw material for the preparation of BeF_2 was $(NH_4)_2BeF_4$. The preparation of $(NH_4)_2BeF_4$ required the reaction of $Be(OH)_2$, ammonia, and

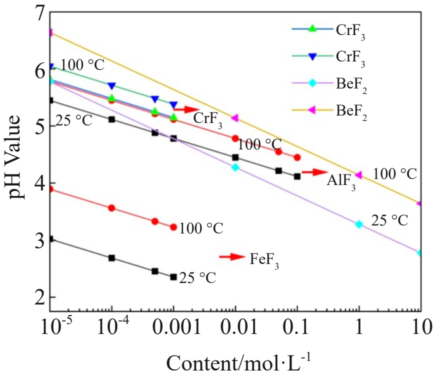


Fig.1 pH ranges of several sulfate precipitates

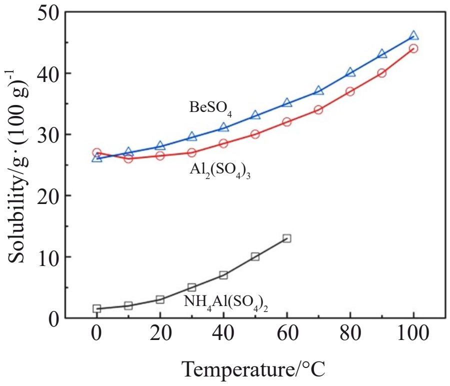


Fig.2 Comparison of Al^{3+} and Be^{2+} solubility

hydrofluoric acid, as expressed by Eq.(9), as follows:

$$Be(OH)_2+2NH_4OH+4HF=(NH_4)_2BeF_4+4H_2O \tag{9}$$

$(NH_4)_2BeF_4$ underwent thermal decomposition, as expressed by Eq.(10), as follows:

$$(NH_4)_2BeF_4=2NH_3+2HF+BeF_2 \tag{10}$$

BeF_2 obtained from thermal decomposition was thermally reduced by magnesium to obtain beryllium metal beads, as expressed by Eq.(11), as follows:

$$BeF_2+Mg=MgF_2+Be \tag{11}$$

Beryllium beads were vacuum-distilled to remove volatile impurity elements, such as zinc and phosphorus, but non-volatile ions, such as Al^{3+}, Cr^{3+}, and Fe^{3+}, remained in beryllium metal.

2.2 Root causes of beryllium metallurgy problems

The technical indexes of modern beryllium metallurgy are shown in Table 2, the international indexes are higher than the indexes from Chinese research, and the metallurgy indexes and product purity need to be improved.

The root cause of the problems, such as a large amount of hazardous waste in the smelting process, low beryllium resource rate, low purity of beryllium products, high energy consumption, etc, results from the theory of beryllium ore purification by sulfuric acid leaching, which is analyzed as follows.

(1) The pH overlap interval required for precipitation of Al^{3+}, Cr^{3+}, and Be^{2+} is large, and thus Al^{3+} and Cr^{3+} cannot be removed by pH precipitation.

(2) The required pH intervals for Fe^{3+} and Be^{2+} precipitation partially overlap, and it is difficult to remove $BeSO_4$ in the iron removal process. Most of the hydroxide precipitation is colloidal, colloid-like, or earthy, which easily entrains the solution, so the Be^{2+} content in iron slag exceeds the standard content.

(3) The solubility of $NH_4Al(SO_4)_2$ cannot be easily distinguished from that of $BeSO_4$, the residual aluminum content in $BeSO_4$ solution is high, the amount of $NH_4Al(SO_4)_2$ is large, and the evaporation and crystallization process entraps the beryllium solution, which leads to excess beryllium in the aluminum slag. In the extraction process, the ratio of beryllium to aluminum is limited, and the aluminum content is still difficult to reduce to a low level.

(4) A large amount of calcite, sulfuric acid, and ammonia was added during the dissociation and purification process to form bulk silicon-calcium mixed slag (white slag), alumina slag, and ammonium sulfate slag, resulting in a ratio of slag to ore in the process exceeding 10. Be^{2+} was entrained in the slag, which not only made the slag difficult to treat, but also caused the decrease in yield rate of beryllium to 70%.

(5) High-temperature tempering calcination not only increases the amount of slag, but also substantially increases the smelting power consumption.

2.3 Transformative beryllium metallurgy (dissociative purification) theory

Since there are so many deficiencies in the sulfuric acid (H_2SO_4) leaching theory, attempts were made to select other leaching systems. Based on the comparison in Fig. 3, it is found that HF leaching can solve the problem of purification by H_2SO_4 leaching, significantly improve the yield rate of beryllium and the purity of beryllium, simplify the purification process, reduce the energy consumption of beryllium metallurgy, and improve the economic efficiency of beryllium metallurgy.

2.3.1 Highly efficient separation and purification by physical method

As listed in Table 3, the solubility of BeF_2 is very high, but the solubility of AlF_3, FeF_3, and CrF_3 is very low. Therefore, it can be considered to change the chemical separation to physical separation.

Assuming that the solubility of the fluoride XF_n is x g·(100 g)$^{-1}$ and the solubility of BeF_2 is y g·(100 g)$^{-1}$, and ignoring the common ion effect, the concentration of the

Table 2 Technical indexes of beryllium metallurgy

Process	Indexes from Chinese research	International indexes
Beryllium ore dissociation technique	Beryllium leaching rate of 92%; slag ore ratio of 10:1	Beryllium leaching rate of 94%; slag ore ratio of 9:1
Research on the separation and purification technique and equipment of beryllium solution	BeO purity of 98.5%; Be recovery rate of 70%	BeO purity of 99.5%; Be recovery rate of 85%
Integrated beryllium utilization rate for whole process/%	50	65
Waste residue resource utilization and disposal technique	-	Recyclable

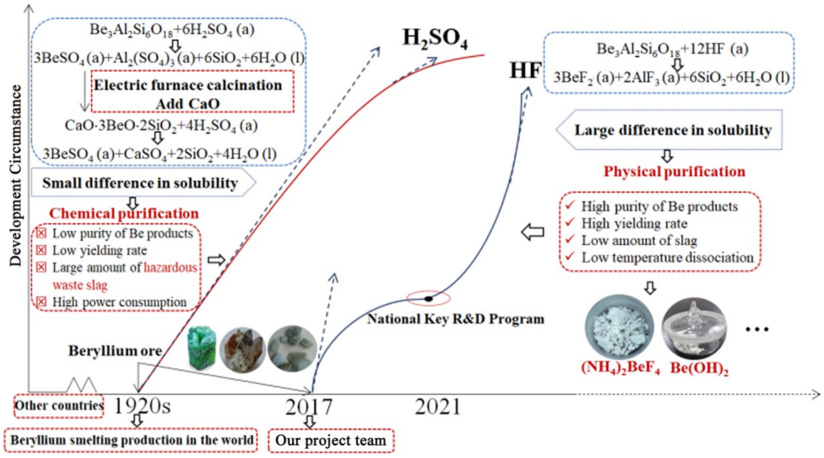


Fig.3 Comparison of beryllium metallurgy theories between sulfuric acid system and hydrofluoric acid system

Table 3 Solubility of different fluorides in water at 25 °C

Fluoride	Solubility in aqueous solution/g·(100 g)$^{-1}$
BeF_2	117.5
AlF_3	0.005
FeF_3	0.07
CrF_3	0.013
CaF_2	0.0016
MgF_2	0.013

fluoride impurity in BeF_2 can be expressed by Eq. (12), as follows:

$$\frac{x}{x+y}\times 100\% \tag{12}$$

If the fluoride system contains multiple fluoride salts (except BeF_2) with solubility of x_1, $x_2 \ldots x_n$, and the individual fluorides are independent from each other with no salting out or common ion effect, the theoretical purity of BeF_2 for physical separation dependent on solubility can be expressed by Eq.(13), as follows:

$$100\% - \frac{\sum_{i=1}^{n} x_i}{y+\sum_{i=1}^{n} x_i}\times 100\% \tag{13}$$

For AlF_3 impurity, x=0.005; for BeF_2, y=117.5.

Then, relying on the solubility separation, the purity of BeF_2 could reach 99.995%, which completely changed the difficult separation problem of $Al_2(SO_4)_3$.

For Fe^{3+}, x=0.07, and for BeF_2, y=117.5. The purity of BeF_2 was 99.95%.

For Cr^{3+}, x=0.013, and for BeF_2, y=117.5. The purity of BeF_2 is 99.98%.

In fact, due to the high concentration of BeF_2 in solution, the concentration of Fe^{3+} and Cr^{3+} can be further decreased by the common ion effect. Thus, there is no need to remove Fe^{3+} and Cr^{3+} by hydroxide precipitation.

In addition, H_2SiF_6 would be formed in the HF leaching process. The boiling point of H_2SiF_6 is low, and the separation of silicon could be achieved by evaporation. H_2SiF_6 could also be recycled to generate HF.

Through a simple physical separation method, the high purity of BeF_2 can be prepared, and the loss of beryllium in the process of chemical precipitation could be reduced. The yielding rate of beryllium in the purification process can be improved, and the amount of waste residue can be reduced.

2.3.2 Thermodynamics of low-temperature leaching of beryllium ore with hydrofluoric acid

The reaction and Gibbs free energy of beryl phase with hydrofluoric acid are expressed by Eq. (14–15), respectively, as follows:

$$\begin{aligned} Be_3Al_2Si_6O_{18}+12HF(a)&=3BeF_2(a)+2AlF_3(a)\\ &+6SiO_2+6H_2O(1) \end{aligned} \tag{14}$$

$$\Delta G^0=-488363-194.5T \tag{15}$$

As a comparison, the reaction and Gibbs free energy of the beryl phase with sulfuric acid are expressed by Eq. (16–17), respectively, as follows:

$$\begin{aligned} Be_3Al_2Si_6O_{18}+6H_2SO_4(a)&=3BeSO_4(a)\\ +Al_2(SO_4)_3(a)&+6SiO_2+6H_2O(1) \end{aligned} \tag{16}$$

$$\Delta G^0=-266841+626.8T \tag{17}$$

In the conventional process of dissociating beryllium ores, calcination in an electric furnace with sulfuric acid leaching was used, and the reaction occurred when a smaller amount of CaO was added, as shown in Eq. (18) as follows:

$$\begin{aligned} 3BeO\cdot Al_2O_3\cdot 6SiO_2+2CaO&=CaO\cdot Al_2O_3\cdot 2SiO_2\\ &+CaO\cdot 3BeO\cdot 2SiO_2+2SiO_2 \end{aligned} \tag{18}$$

With the continuous addition of CaO, the eaction occurs, as shown in Eq. (19), as follows:

$$\begin{aligned} 3BeO\cdot Al_2O_3\cdot 6SiO_2+4CaO&=CaO\cdot Al_2O_3\cdot 2SiO_2\\ &+CaO\cdot 3BeO\cdot 2SiO_2+2CaO\cdot SiO_2 \end{aligned} \tag{19}$$

Then, continuously adding CaO, the following reaction occurs:

$$3BeO\cdot Al_2O_3\cdot 6SiO_2+6CaO=3BeO\cdot Al_2O_3+6CaO\cdot SiO_2 \tag{20}$$

According to these reactions, it can be seen that the beryllium-containing products include $CaO\cdot 3BeO\cdot 2SiO_2$ and $3BeO\cdot Al_2O_3$, which can react under hydrofluoric acid system and sulfuric acid system, respectively. The reactions and corresponding Gibbs free energies are expressed in Eq.(21–28), as follows:

$$3BeO\cdot Al_2O_3 + 6H_2SO_4(a) = 3BeSO_4(a) + Al_2(SO_4)_3(a) + 6H_2O(l) \tag{21}$$

$$\Delta G^0 = -313769 + 276.2T \tag{22}$$

$$3BeO\cdot Al_2O_3 + 12HF\ (a) = 3BeF_2\ (a) + 2AlF_3\ (a) + 6H_2O\ (l) \tag{23}$$

$$\Delta G^0 = -714860 - 156.4T \tag{24}$$

$$CaO\cdot 3BeO\cdot 2SiO_2 + 4H_2SO_4(a) = 3BeSO_4(a) + CaSO_4 + 2SiO_2 + 4H_2O(l) \tag{25}$$

$$\Delta G^0 = -182250 + 22.1T \tag{26}$$

$$CaO\cdot 3BeO\cdot 2SiO_2 + 8HF(a) = 3BeF_2(a) + CaF_2 + 2SiO_2 + 4H_2O(l) \tag{27}$$

$$\Delta G^0 = -414411 - 470.9T \tag{28}$$

As shown in Fig.4, HF dissociates the beryl phase with the Gibbs free energy of −500 kJ·mol^{-1}, which thermodynamically allows the reaction to proceed adequately. However, the direct dissociation of the beryl phase with H_2SO_4 results in a small absolute value, although the Gibbs free energy was also less than 0. In the standard state, the value of the Gibbs free energy increases as the reaction temperature increases, especially when the reaction temperature is higher than 160 °C, and the reaction proceeds in the reverse direction. As a comparison, the absolute value of the Gibbs free energy of sulfuric acid leaching of the $CaO\cdot 3BeO\cdot 2SiO_2$ phase is also significantly lower than that of the direct reaction of HF with the beryl phase, which shows that hydrofluoric acid leaching has a clear advantage from a thermodynamic point of view. With sulfuric acid, beryl requires high temperature to destroy the structure of beryl phase; while for hydrofluoric acid, beryllium ore can be dissociated directly at low temperature, realizing the theories of high temperature calcination of calcite (approximately 1500 °C)+sulfuric acid leaching and low temperature hydrofluoric acid direct leaching.

Hydrofluoric acid can also react with SiO_2 in the leaching process, as expressed by Eq.(29–30), as follows:

$$SiO_2 + 6HF\ (a) = H_2SiF_6\ (a) + 2H_2O\ (l) \tag{29}$$

$$\Delta G^0 = -83637 + 94.9T \tag{30}$$

The reactions can be obtained from thermodynamic equilibrium, as follows:

$$a_{H_2SiF_6} > a_{HF}^6 \cdot \exp\left(\frac{-\Delta G^0}{RT}\right) \tag{31}$$

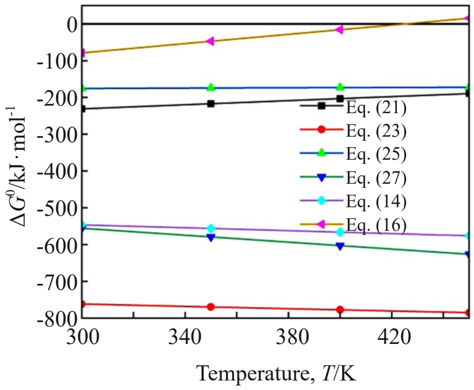


Fig.4 Thermodynamic comparison of dissociated beryllium ore in different systems

According to the relationship in Fig.5, the reaction of SiO_2 and hydrofluoric acid in beryllium ore can be inhibited by adjusting the solution temperature and HF concentration as well as artificially adding H_2SiF_6.

2.3.3 Hydrofluoric acid leaching kinetics of beryllium ore at low temperature

The process of leaching beryllium ore powder under the hydrofluoric acid system can be simulated by the shrinking core model, as expressed by Eq.(32), as follows:

$$\frac{6\rho_{BeO} r_0}{3(c_0 - Rn_0/V)}\cdot\frac{dR}{d\tau} = k(1-R)^{\frac{2}{3}} \tag{32}$$

where leaching rate is defined as R; the concentration before reaction is c_0, considering that the concentration of HF in the solution changes dynamically as the reaction proceeds; n_0 is the HF content (mol) consumed for the completion of the reaction; ρ_{BeO} is the BeO volumetric molar density of the ore powder (mol/m^3); k is the rate constant of the interfacial chemical reaction (m/s); r and r_0 are the inner and outer diameters of the nuclear model, respectively. The effect of ore powder particle size on the dissociation rate is shown in Fig.6.

After the kinetic tests (leaching at 120 °C for 2 h), 99% Be^{2+} can be leached from beryllium ore powder with particle size of 0.075 mm. With the refinement of particles, the reaction rate is accelerated. For beryllium ore powder with size above 0.019 mm, the reaction can be conducted without a

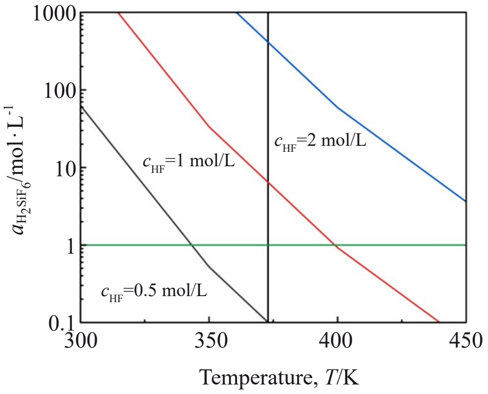


Fig.5 Diagram of metallurgy conditions required for formation of fluorosilicic acid

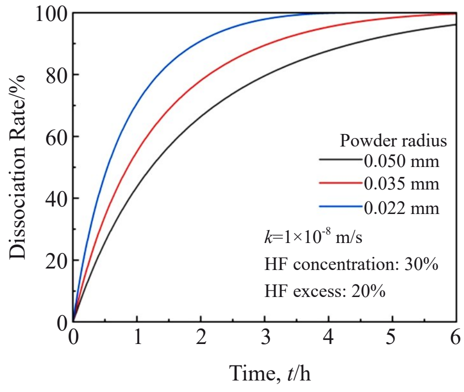


Fig.6 Effect of particle size of ore powder on dissociation rate

heat source, the reaction process between hydrofluoric acid and beryllium ore powder is a self-heating process, and the temperature of the solution can be maintained at 70–90 °C.

It can be seen that the reaction temperature of the hydrofluoric acid leaching system is much lower than the concentrated sulfuric acid leaching temperature (approximately 200 °C), so the self-heating reaction can be realized, which not only reduces the energy consumption in the dissociation process, but also decreases the energy consumption in the melting process link of the electric furnace.

2.3.4 Preparation of $Be(OH)_2$

After the preparation of BeF_2 solution, BeF_2 can be obtained by drying and calcining. BeF_2 can be used as a raw material to prepare metal beryllium and beryllium alloy.

In addition, the beryllium industry has BeO ceramics and therefore requires $Be(OH)_2$. BeF_2 is formed and then the pH can be adjusted by ammonia to produce a $Be(OH)_2$ precipitate.

In the sulfate system, H_2SO_4 is a strong acid, and soluble sulfate is a strong electrolyte. However, in the fluoride system, HF is a weak acid; BeF_2 and AlF_3 are weak electrolytes; FeF_3 and CrF_3 are strong electrolytes. Thus, the pH value of the hydroxide precipitation is quite different from that of the sulfate system. As shown in Fig. 7, the pH value of BeF_2 to form $Be(OH)_2$ precipitation can be well separated from the pH range of FeF_3, CrF_3, and AlF_3 to form hydroxide precipitation, and this theory facilitates the deep removal of Fe^{3+} and Cr^{3+} ions in the BeF_2 solution. So the purity of beryllium can reach the level of 4N–5N grade.

3 Changes in Beryllium Ore Metallurgy Methods

3.1 Modern beryllium metallurgy method

The modern beryllium metallurgy method is formulated according to the theory of sulfuric acid dissociation and purification, and the main processes include electric furnace melting, H_2SO_4 leaching, $NH_4Al(SO_4)_2$ preparation, evaporation+crystallization, the removal of Fe from the crude $BeSO_4$ solution using pH precipitation, precipitation of $Be(OH)_2$, calcination of BeO, the preparation of $(NH_4)_2BeF_4$, calcination of $(NH_4)_2BeF_4$, thermally reduced beryllium beads of BeF_2, and the processing of a wide range of metallic beryllium alloys and BeO ceramics from $Be(OH)_2$, as shown in Fig. 8. The process indexes are listed in Table 4.

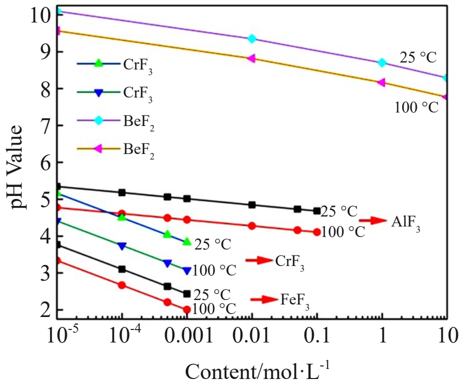


Fig.7 pH range for conversion of different fluorides to hydroxide precipitates

3.2 Transformative method of beryllium metallurgy

The beryllium metallurgy change method is based on the beryllium metallurgy theory of change[31–35]. The main processes are low-temperature (room temperature) dissociation of beryllium ore, evaporation of dissociation solution to remove H_2SiF_6 and excess HF, low-temperature calcination of beryllium-containing fluoride, room-temperature dissolution of beryllium-containing fluoride to isolate impurities (such as AlF_3 and FeF_3), calcination of water-containing BeF_2 for the preparation of pure BeF_2, chemical precipitation of BeF_2 solution for the preparation of $Be(OH)_2$, HF regeneration from H_2SiF_6, as well as the preparation and processing of BeO ceramics, metallic beryllium, and beryllium alloy. According to the process flow in Fig. 9, beryllium ore and HF were leached in the reactor at low temperature to obtain the

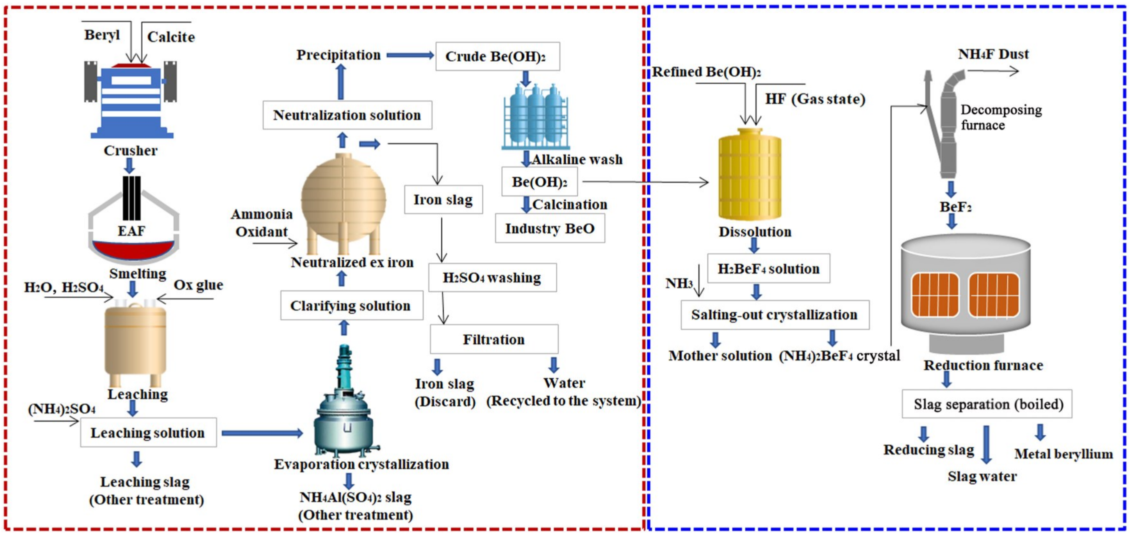


Fig.8 Modern beryllium metallurgical process

Table 4 Comparison of modern beryllium metallurgy (dissociation and purification) and transformation methods

No.	Project type	Sub-project type	Existing process	Transformative process
1	Main methods and indexes of dissociation process	High-temperature device	High temperature melting dissociation (arc-melting)	-
		Acid leaching medium	H_2SO_4	HF
		Leaching temperature	200 °C	Dissociation at low temperature or without external heating
		Dissociation yield/%	94	99
2	Purification process, main methods, and indicators	Purification method	Chemistry	Physics
		Main methods and equipment	Ammonium sulfate, evaporation, concentration, crystallization reactor, or extraction pH adjustment with ammonia to remove impurities, such as iron and aluminum	Evaporation to remove H_2SiF_6 (evaporation kettle) Dissolving at room temperature to remove impurities, such as AlF_3, FeF_3, and MnF_2
3	Types and indicators of dissociation purified products	Beryllium products	$Be(OH)_2$	BeF_2
		Purity	98%–98.5%	99.5%–99.9%; BeF_2 (3N–5N grade) can be prepared by chemical method in the BeF_2 refining chain
		Comprehensive recovery rate/%	75	95
4	Other major Be products processing	Beryllium product type	BeF_2	$Be(OH)_2$
		Processing method	$Be(OH)_2+2NH_4OH+4HF=(NH_4)_2BeF_4+4H_2O$	Formation of $Be(OH)_2$ precipitate by adjusting the pH of BeF_2 solution with ammonia
		Product purity/%	99.0–99.5	99.9–99.999
5	Metal beryllium bead processing and indicators	Equipment	High temperature induction furnace	Low temperature reduction+distillation
		Be direct yield/%	<60	>85
		Be purity/%	98	99.9–99.999
6	Environmental protection	Slag:ore ratio	>10:1	<2:1
		Types of slag	Silicon slag, alum slag, iron slag, neutralization slag, and Be bead reduction slag	White carbon black, ammonium sulfate, AlF_3, and MgF_2
		Is it a hazardous waste or a product	Hazardous waste; high treatment costs	Products, environmentally friendly
7	Whole plant situation	Comprehensive yield rate of Be in the whole plant/%	50	90
		Product purity	General	High-grade
		Energy consumption and carbon emissions	High	Less
		Investment	Large	Small
		Economy	Small	Large

beryllium-containing solution, which realized the low-temperature dissociation of beryllium ore. Then, the beryllium-containing solution after liquid-solid separation was evaporated to remove HF. In addition, during the pre-leaching reaction, part of SiO_2 reacts with HF to form H_2SiF_6, and most H_2SiF_6 will be removed in the evaporation process because of the low boiling point of H_2SiF_6 and the obvious volatilization above 100 °C. Finally, in this research, the low-temperature calcination method was chosen to destroy the structure of the complexed acids (H_2FeF_6, H_2AlF_6), so the difference in fluoride solubility can be effectively utilized for physical separation in the later stages. The residual H_2SiF_6 is also

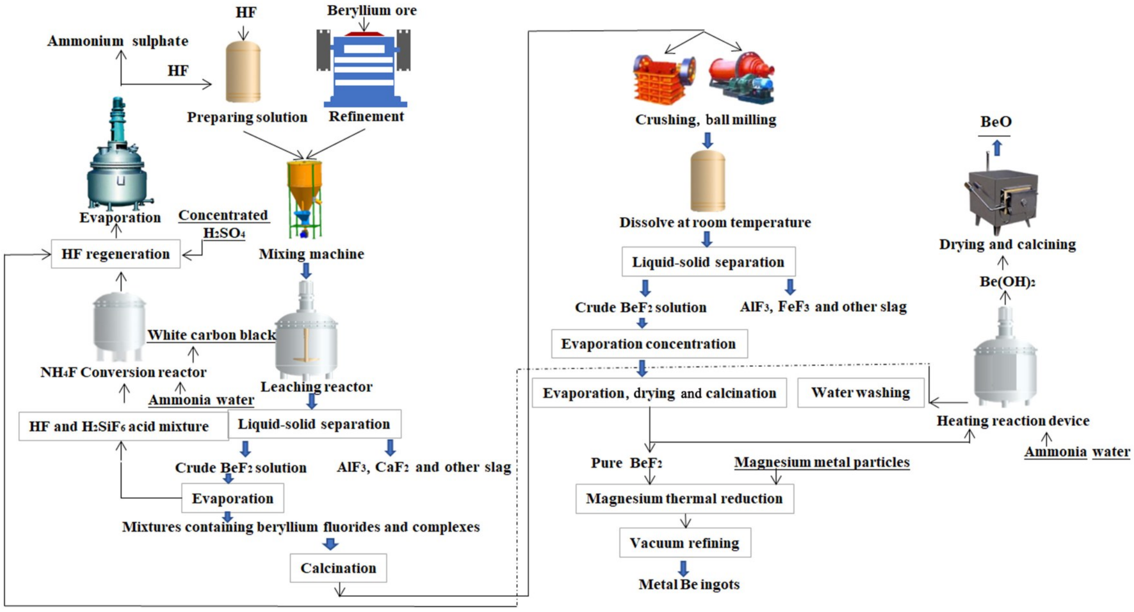
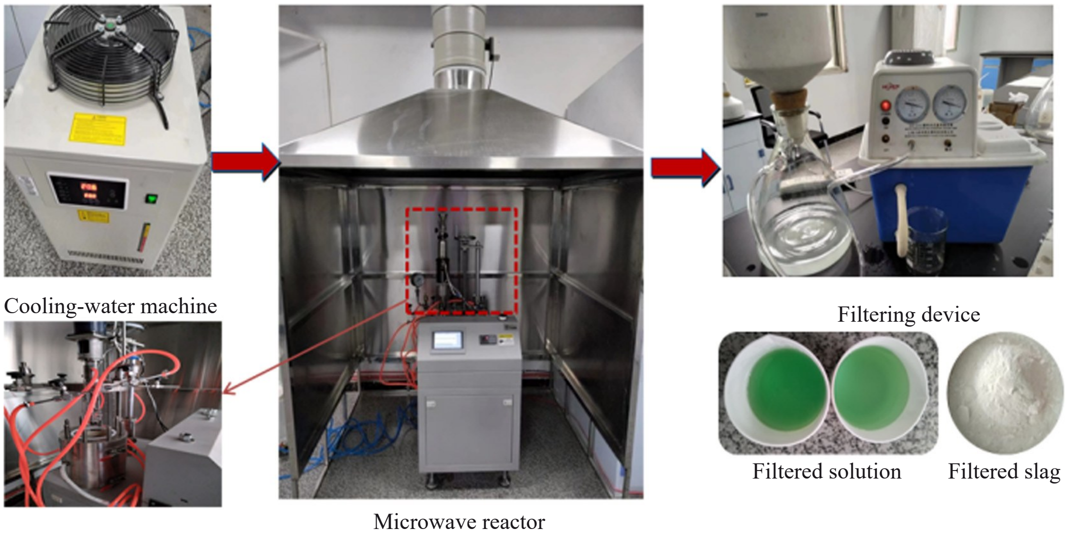


Fig.9 Beryllium metallurgy transformation method and process flow


Cooling-water machine

Microwave reactor

Filtering device

Filtered solution

Filtered slag

Fig.10 Experimental platform for the microwave reaction for the dissociation of beryllium ore by hydrofluoric acid

removed by evaporation in the calcination step.

The process technical indicators of the transformative method are shown in Table 4. In addition to the subversive changes in the beryllium ore dissociation and purification methods, the method also has many technological advances in the high-efficiency reduction of beryllium beads and by-products, resulting in higher beryllium yield rate, environmentally friendly utilization of slag, and better economics.

The beryllium fluoride and beryllium hydroxide products with purity of 99.9% have been synthesized using the test rig (Fig. 10) and the method described in this research, and the resultant composition is shown in Table 5.

Table 5 Chemical composition of impurities in BeF_2 and $Be(OH)_2$

Type	Fe/wt%	Al/wt%	Mn/wt%	Mg/wt%	Purity/%
BeF_2	0.015	0.014	0.007	0.009	99.91
$Be(OH)_2$	0.011	0.012	0.006	0.007	99.93

4 Conclusions

1) Modern beryllium metallurgy (dissociation and purification) methods are based on the theory of sulfuric acid dissociation and chemical purification. The high solubility of sulfate produced by sulfuric acid dissociation and the separation conditions of the chemical method highly overlap, which leads to low purity of the product, presence of beryllium ions in the separated phase, and hazardous waste, thus lowering the beryllium yield rate. The direct dissociation rate of beryllium ore sulfate is low, and destroying the

structure of beryllium ore by electric furnace plus calcite not only substantially increases the amount of slag, but also substantially increases the consumption of electricity and CO_2 emissions.

2) A transformative beryllium metallurgy theory based on the low-temperature dissociation of hydrofluoric acid and purification by the high variability of fluoride solubility is proposed. Hydrofluoric acid can quickly dissociate beryllium ore powder directly at low temperature or room temperature. The dissociation rate is more than 99%, the impurities, such as AlF_3, FeF_3, CrF_3, CaF_2, and MgF_2, have low solubility, and the common ion effect exists in the system, which results in beryllium products of 99.9% purity without chemical purification. For high-purity beryllium products of 4N grade or even higher, high-purity Be can be prepared by the superior property that the pH intervals of Fe, Cr, and other hydroxide precipitates are significantly different from those corresponding to $Be(OH)_2$ precipitates.

3) A new beryllium metallurgy method and process based on the theory of low-temperature dissociation and purification of hydrofluoric acid was proposed. This metallurgy process can prepare a wide range of beryllium products that are prepared by the modern beryllium metallurgy process. It has significant technological advances in several aspects, such as high beryllium product purity, large beryllium yield, as well as low-carbon and environmentally friendly preparation.

References

1 Zhang Jianfu, Yu Yipeng. *Modern Transportation and Metallurgical Materials*[J], 2021, 1(6): 76 (in Chinese)

2 Yang C, Wu B, Deng W *et al*. *Crystals*[J], 2023, 13(9): 1330

3 Xu Demei, Li Meitu, Dai Yanming *et al*. *Rare Metal Materials and Engineering*[J], 2022, 51(8): 2971 (in Chinese)

4 China Nonferrous Metals Industry Association Expert Committee. *Beryllium Industry in China*[M]. Beijing: Metallurgical Industry Press, 2015 (in Chinese)

5 Wang Jing, Peng Shixian, Wang Min *et al*. *Rare Metal Materials and Engineering*[J], 2023, 52(8): 2901 (in Chinese)

6 Zhu Xuehong, Feng Hui, Zhang Hongwei. *Journal of Central South University* (*Social Science Edition*) [J], 2023, 29(5): 138 (in Chinese)

7 Shao Weihua, Zeng Yongjie, Chang Xueyong *et al*. *Conservation and Utilization of Mineral Resources*[J], 2023, 43(1): 98 (in Chinese)

8 Xu Demei, Li Feng, Li Meitou *et al*. *Rare Metal Materials and Engineering*[J], 2023, 52(8): 2819 (in Chinese)

9 Zheng F L, Wang G X, Yue N L *et al*. *Materials Science Forum*[J], 2020, 977: 261

10 He Lijun, Fang Hui, Li Meitu *et al*. *Rare Metal Materials and Engineering*[J], 2019, 48(12): 3954 (in Chinese)

11 Chen Z, Jin G, Chen K *et al*. *Fusion Engineering and Design*[J], 2013, 88(12): 3280 (in Chinese)

12 He Lijun, Xu Demi, Hu Nan *et al*. *Rare Metal Materials and Engineering*[J], 2014, 43(3): 567 (in Chinese)

13 Ren Penghe, Xiao Lairong, Cai Zhenyang *et al*. *Rare Metal Materials and Engineering*[J], 2023, 52(4): 1267

14 Liang Fei. *Characterization of Beryllium Resources, Supply and Demand Prediction and Development Discussion in China*[D]. Beijing: Chinese Academy of Geological Sciences, 2018 (in Chinese)

15 Huang Leiming, Wu Yanni, Wei Xiangsong *et al*. *Geology of Chemical Minerals*[J], 2022, 44(1): 93 (in Chinese)

16 Xiao Chao, Li Jie, Wu Haiguo. *Rare Metals and Cemented Carbides*[J], 2013, 41(3): 8 (in Chinese)

17 Lei X. *Hunan Nonferrous Metals*[J], 2004, 20(1): 21 (in Chinese)

18 Xu Q, Yang L, He S *et al*. *Materials Letters*[J], 2020, 274: 963

19 Da P D F, André O, Marcos V D S R *et al*. *Ceramics International*[J], 2023, 49(18): 29647

20 Zhou Yanjun, Song Kexing, Mi Xujun *et al*. *Rare Metal Materials and Engineering*[J], 2018, 47(4): 1096

21 Shi Yulong. *Research on High-Level BeO Substrate for Microwave Monolithic Ceramic Circuits*[D]. Chengdu: University of Electronic Science and Technology of China, 2017 (in Chinese)

22 Zhang Shaohua, Zhong Chaobit, Zhang Shuren *et al*. *Electronic Components and Materials*[J], 2010, 29(8): 11 (in Chinese)

23 Zhong Jingming, Xu Demei, Li Chunguang *et al*. *Materials China*[J], 2014, 33(Z1): 568 (in Chinese)

24 Ito T, West J. *Zeitschrift für Kristallographie*[J], 2014, 83(1–6): 384

25 Ripp S G, Izbrodin A I, Lastochkin I E *et al*. *Geochemistry International*[J], 2016, 54(9): 748

26 Samoilov I V, Bekimbaeva S G, Onalbaeva S Z *et al*. *Russian Journal of Applied Chemistry*[J], 2016, 89(2): 185

27 Dean J A. *Lange's Handbook of Chemistry*[M]. Beijing: Science Press, 2003 (in Chinese)

28 Editorial Board of the Handbook of Rare Metals. *Handbook of Rare Metals*[M]. Beijing: Metallurgical Industry Press, 2008 (in Chinese)

29 Everest D A. *The Chemistry of Beryllium*[M]. Amsterdam: Elsevier, 1964

30 Yao Yunbin. *Handbook of Physical Chemistry*[M]. Shanghai: Shanghai Science and Technology Publisher, 1985 (in Chinese)

31 Guo Peimin, Zhao Pei, Wang Lei. *Chinese Patent*, CN112322893A[P], 2021 (in Chinese)

32 Guo Peimin, Wang Lei, Kong Lingbing *et al*. *Chinese Patent*, CN113003591A[P], 2021 (in Chinese)

33 Guo Peimin, Zeng Zhiyan, Wang Lei *et al*. *Chinese Patent*, CN113059154B[P], 2022 (in Chinese)

34 Guo Peimin, Wang Lei, Kong Lingbing *et al*. *Chinese Patent*, CN112794343B[P], 2022 (in Chinese)

35 Shen Yaozong, Guo Peimin, Wang Lei *et al*. *Nonferrous Metals* (*Extractive Metallurgy*)[J], 2023(10): 42 (in Chinese)

铍矿变革性冶金(解离纯化)理论及方法

郭培民[1,2]，申耀宗[1,2]，王　磊[1,2]，孔令兵[1,2]，王东新[4]，郭　庆[3]
(1. 钢铁研究总院有限公司 先进钢铁流程及材料国家重点实验室，北京 100081)
(2. 钢研晟华科技股份有限公司，北京 100081)
(3. 五矿铍业股份有限公司，湖南 衡阳 421513)
(4. 西北稀有金属材料研究院宁夏有限公司，宁夏 石嘴山 753000)

摘　要：提出了基于氢氟酸低温解离和利用氟化物溶解度差异性大的特点进行纯化的变革性铍冶金理论和方法，氢氟酸可直接在低温或室温下快速解离铍矿粉，解离率超过99%，AlF_3、FeF_3、CrF_3及MgF_2等氟化物溶解度低，再加上同离子效应，无需化学纯化即可制备纯度为99.9%的铍产品。对于4N级以上的高纯铍产品，则可利用铁、铬等氢氧化物沉淀的pH区间明显不同于$Be(OH)_2$沉淀所对应的pH区间的优越特性进行高纯铍的制备。这一方法可用于制备现代铍冶金可制备的大部分铍产品。

关键词：铍矿冶金；硫酸；氢氟酸；纯度；收得率；环保

作者简介：郭培民，男，1975年生，博士，教授级高级工程师，钢铁研究总院有限公司先进钢铁流程及材料国家重点实验室，北京 100081，E-mail：guopm@pku.org.cn