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Kinetic Mechanism in the Process of Carbothermal Reduction of Ferrum Niobate

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Abstract: Ferrum niobate was synthesized by solid-phase sintering method in a vacuum carbon tube furnace at 1 300 ℃ for 180 min. The phase transformation of ferrum niobate carbothermal reduction process was studied by XRD. The reduction reactions of ferrum niobate in different temperature stages were determined by the TG-DSC curve. Meanwhile, according to the TG curve, the reaction kinetics parameters were calculated by A.W.Coats integration and the control steps in different temperature stages were ascertained. The results showed that the reduction of ferrum niobate starts at the temperature of 1 000 ℃, and the reduction process carries out in two steps according to sintering temperature.In a temperature range of 1 000-1 238 ℃ (the first step), the main reduction products are NbO_2 and Fe; the kinetic equation of initial stage is $[-\ln(1-\alpha)]^4=kt$, controlled by nucleation growth, and the apparent activation energy is 388 kJ/mol; with the temperature increasing, the kinetic equation is $\alpha+(1-\alpha)\ln(1-\alpha)=kt$, which is the Valensi two-dimensional diffusion kinetic equation, and the apparent activation energy is 264.4 kJ/mol. The main reaction in a range of 1 238-1 344 ℃(the second step) is the reduction of NbO_2 to NbC, the kinetic equation is $[(1-\alpha)^{-1/3}-1]^2=kt$, which is controlled by the three-dimensional diffusion, and the apparent activation energy is 482.7 kJ/mol.

Key words: ferrum niobate; carbothermal reduction; kinetics

1 Introduction

Niobium is a kind of important rare metal. In recent years, special columbic alloys have been developed rapidly with the advancement of technology and the urgent demand for special materials. There are abundant resourse of niobium in China, and the BayanObo mineral deposit has the largest reserves which accounts for more than 90% of the total niobium reserves. However, niobium minerals have many types, low content, fine embedding, and complex occurrence states. So, it is difficult to directly obtain niobium products from raw ores[1]. The characteristic of niobium mineralization is highly decentralized occurrence, however, about 80% of niobium minerals concentrate in twelve types of niobium minerals. In these minerals, niobite, fersmite, ilmenorutile, pyrochlore and aeschynite can be used for separation[2].

In all the niobium containing minerals of BayanObo mineral, niobite which consists mainly of ferrum niobate, contains the highest content of niobium and the largest distribution. The recent research showed that blast furnace reduction, electric furnace smelting and stereoselective reduction all aim to reduce niobite to niobium oxides or carbides in pyrometallurgy technology of niobium extraction,and in the next step of smelting, niobium oxides in the rich niobium slag are reduced and enter into molten iron to generate ferrocolumbium[3,4]. Because of the low content of niobium and complex phase, the reduction temperature of niobium minerals and the reactions in this temperature range can not be controlled accurately. If the temperature of each step reaction in the reduction course of the niobium minerals can be judged accurately, it will shorten technological process and reduce energy consumption.

In this article, ferrum niobate was synthesized

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by the method of solid state sintering and the phase transformation in the carbothermal process was investigated. Furthermore, the reduction kinetics mechanism of ferrum niobate was studied under non-isothermal condition by TG-DSC method, then the kinetic parameters were calculated, and the control steps of different temperature range were determined. It provides a theoretical basis for actual production of the pyrometallurgy niobium extraction technology.

2 Experimental

2.1 Materials

Niobium pentoxide, purity≥ 99.5 %; Iron trioxide, purity≥ 99.5 %; Activated carbon, purity≥ 98.5%.

2.2 Equipments

Vacuum carbon tube furnace (ZT-50-20 type, Shanghai ChenRong Electric Stove Limited Company, the power is 50 kW and the vacuum is less than 10 Pa); synthetical thermal analysis instrument (STA499A F3 type, NETZSCH); X-ray powder diffractometer(PW-1700, Dutch Philips Company, incidental electorate energy spectrum);scanning electron microscope(S-3400N, Japan Hitachi Company); X-ray energy loss spectrometer (FEI Company Sinion 200 FESEM Oxfond Instruments).

2.3 Solid-phase synthesis of ferrum niobate

The reaction equation of ferrum niobate synthesis[5] is

$$2Fe_2O_3 + 4\,Nb_2O_5 = 4Fe\left(NbO_3\right)_2 + O_2 \qquad (1)$$

Nb_2O_5 and Fe_2O_3 were weighed by stoichiometric ratio according to Eq.(1). The solid-state synthesis reaction was conducted, heating to 1 300 ℃ and keeping constant temperature for 3 hours in the vacuum carbon tube furnace under the protection of argon gas, and then cooled to room temperature in the furnace. The sample was analyzed by XRD and SEM, and the results are shown in Fig.1 and Fig.2.

Table 1 EDS of synthetical ferrum niobate

Element	Quality fraction/%			Atom fraction/%		
	A	B	C	A	B	C
Nb	54.23	57.63	61.23	21.64	24.55	24.53
Fe	16.77	16.65	16.59	11.11	11.78	11.68
O	29	25.72	22.18	67.25	63.67	63.79

The XRD result indicates that the black gray samples are pure ferrum niobate. The energy dispersive spectrum (EDS) of SEM was produced on the A B C three points. The compositions are all Fe, Nb and O. As is shown in Table1, the atom ratio of the three elements is approximately 1:2:6 and the synthesized material is ascertainable to be $FeNb_2O_6$.

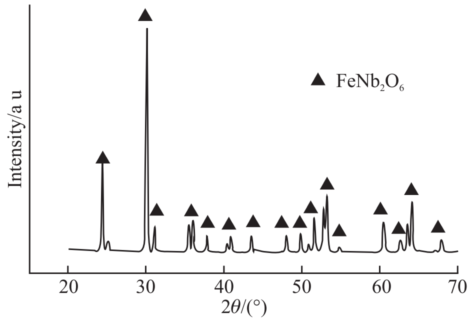

Fig.1 XRD pattern of the syntheitical ferrum niobate

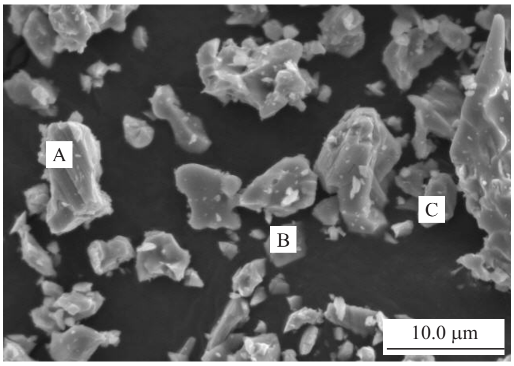

Fig.2 SEM of the synthetical ferrum niobite

3 Results and discusion

3.1 Thermodynamic analysis of the ferrum niobate carbothermal process

Carbothermal reduction products of ferrum niobate possibly include Fe, Nb_2O_5, NbO_2, NbO and NbC. According to the different valences of niobium in different states, niobium can generate several oxides with oxygen. In Nb-O system, the existing major oxides are Nb_2O_5, NbO_2, and NbO, and carbon oxides are mainly CO and CO_2. The Gibbs free energies are as follows[6].

$$\begin{gathered} C_{(s)} + 0.5O_{2(g)} = CO_{(g)} \\ \Delta_f G_m^\theta = -114\,390 - 85.8T \end{gathered} \qquad (2)$$

$$\begin{gathered} C_{(s)} + O_{2(g)} = CO_{2(g)} \\ \Delta_f G_m^\theta = -395\,388 + 0.08T \end{gathered} \qquad (3)$$

$$\begin{gathered} Nb_{(s)} + 0.5O_{2(g)} = NbO_{(s)} \\ \Delta_f G_m^\theta = -414\,216 + 81.6T \end{gathered} \qquad (4)$$

$$\begin{gathered} Nb_{(s)} + O_{2(g)} = NbO_{2(s)} \\ \Delta_f G_m^\theta = -783\,663 + 166.9T \end{gathered} \qquad (5)$$

$$\begin{gathered} 2Nb_{(s)} + 2.5O_{2(g)} = Nb_2O_{5(s)} \\ \Delta_f G_m^\theta = -1\,888\,240 + 417.2T \end{gathered} \qquad (6)$$

$$Nb_{(s)} + C_{(s)} = NbC_{(s)} \qquad (7)$$

$$\Delta_f G_m^\theta = -136\ 900 + 2.4T$$

The above equations show that niobium oxides with lower valence are more stable than niobium oxides with higher valence at the same temperature. According to the oxygen potential of each niobium oxide, Nb_2O_5 is reduced step by step. Firstly, Nb_2O_5 is reduced to NbO_2, secondly, NbO_2 is reduced to NbO, and thirdly, NbO is reduced to NbC. In the actual reaction process, although NbO is very difficult to be reduced by carbon, it is easy to be reduced to NbC by carbon at a lower temperature. However, NbC can not be reduced by carbon in the standard state.

3.2 The phase transformation and TGA of ferrum niobate carbothermal process

Ferrum niobate and activated carbon were weighed stoichiometric ratio according to the Eq.(8):

$$2Fe(NbO_3)_2 + 8C = Fe + 2\,NbC + 6CO \qquad (8)$$

To ensure sufficient reduction, the carbon was over-dosed by 15%. Take the same quantity of mixed samples (5 g) then heat up from room temperature to selected temperature respectively, and cool down to room temperature after 180 min. The XRD results are given in Fig.3.

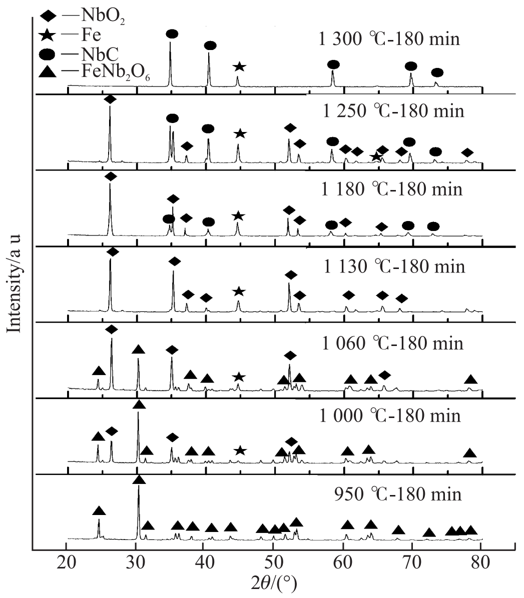

Fig.3 X-ray diffraction patterns under different reduction temperature

As is shown in Fig.3, with the temperature increasing, the diffraction peaks of $FeNb_2O_6$ gradually weaken. However, the diffraction peaks of Fe and NbO_2 strengthen.When the sample was heated to 950 ℃ ,there was no obvious phase transformation happend. It indicates that ferrum niobate carbothermal process does not occur below 950 ℃.There is Fe phase when the temperature rises to 1 000 ℃.When the temperature increases to 1 130 ℃, the diffraction peaks of $FeNb_2O_6$ disappear completely and $FeNb_2O_6$ are all reduced into Fe and NbO_2. As can be concluded, the main reaction in the temperature range of 1 000-1 130 ℃ is the reduction of $FeNb_2O_6$ to Fe and NbO_2. There are abundant NbO_2 and a minute quantity of NbC reduced from NbO_2 at 1 180 ℃. In the temperature range of 1 180-1 300 ℃, the diffraction intensity of NbO_2 gradually weakens, however, the diffraction intensity of NbC gradually strengthens with the temperature increasing. From the above analysis, it is obvious that the first step reaction is ferrum niobate being reduced to NbO_2. Moreover, with the temperature increasing, the reduction product is NbC. It is not tested as the description of theoretical analysis that the first reduction product is Nb_2O_5 and next NbO_2 and then NbO, finally is NbC.

To find out the temperature range of the phase transformation in the carbothermal process of ferrum niobate, TG-DSC analysis was adopted. The $FeNb_2O_6$ samples with the same carbon contents were taken to be analyzed by TG and the results are illustrated in Fig.4.

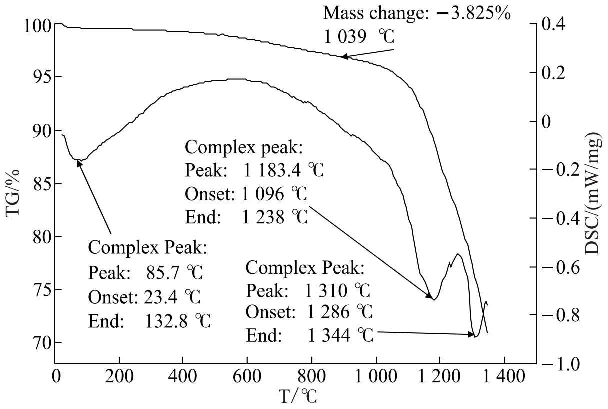

Fig.4 TG-DSC curves of carbothermal reduction of ferrum niobite

The DSC curve in Fig.4 shows that the reaction of sample is endothermic from the start temperature to aim temperature and there are three obvious endothermic peaks. There is an endothermic peak near 86 ℃ attributed to evaporation decalescence of free water absorbed by activated carbon. There is a large endothermic peak near 1 183 ℃ with a temperature range of 150 ℃ and the weight loss rate reaches the maximum. It can be seen that ferrum niobate undergoes carbothermal reaction in this temperature range. There appears another endothermic peak near 1 310 ℃. The intensity of this endothermic peak is higher than the intensity of endothermic peak near 1 183 ℃, however, the peak width is smaller than the former peak.

Additionally, the two endothermic peaks are very close together and the first endothermic peak enters into the next before returning to the baseline, because the temperatures of ferrum niobate being reduced to NbO_2 and NbO_2 being reduced to NbC are close.

It can be seen from Fig.4 that the weight loss percentage is very small and less than 3% below 1 000 ℃. Combined with Fig.3, ferrum niobate has not been reduced below 950 ℃ because the sample loses crystal water in the heating process. After the temperature rises to 1 000 ℃, the slope of the weight loss curve increases rapidly. Combined with Fig.3, the ferrum niobate is reduced by carbon in this temperature range and the reaction speed is very high. The weight loss still continues at 1 350 ℃ because the reactants can react with the corundum crucible and then destroy the reaction system. So, the temperature can not exceed 1 350 ℃.

It can be seen from the TG curve in Fig.4 that the weight loss percentage is 16.55% when the temperature is up to 1 238 ℃. If ferrum niobate is reduced to Fe and NbO_2 completely, the theoretical weight loss percentage is 12.91%. With the addition of dehydration *etc*. factors, the weight loss of the sample is 3.825% (1 039 ℃)which is consistent with the weight loss percentage of 16.55% at 1 238 ℃. Combined with DSC curve and XRD pattern in Fig.3, it can be ascertained that the main reaction is the reduction of ferrum niobate to Fe and NbO_2 in the temperature range from 1 000 to 1 238 ℃.

It can be seen from Fig.3 that a small quantity of NbC produces at 1 180 ℃ and the sample is reduced to Fe and NbC completely at 1 300 ℃. Combined with the DSC curve in Fig.4, the main reaction in the temperature range of 1 238-1 344 ℃ is the reduction of NbO_2 to NbC.

3.3 Kinetic calculation of ferrum niobate carbothermal reduction process

According to the weight loss data from Fig.4, the A.W.Coats method[7,8] was adopted to calculate the kinetic parameters of ferrum niobate carbothermal reduction reaction.

The A.W.Coats integration is described as Eq.(9):

$$\ln\frac{G(\alpha)}{T^2}=\ln\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \tag{9}$$

In this equation, α is the reaction fraction of the reduction process; $G(\alpha)$ is a specific mechanism function model.

Different mechanism functions are substituted into the equation[8] and then the diagram of $\ln[G(\alpha)/T^2]$-$1/T$ is drawn. The method of fitting is adopted to calculate the slope and intercept, so the activation energy can be calculated and the control step can also be ascertained.

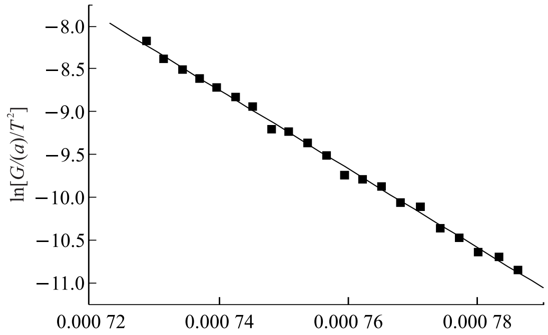

Fig.5 Carbothermal curve of ferrum niobate from 1 000 to 1 096 ℃

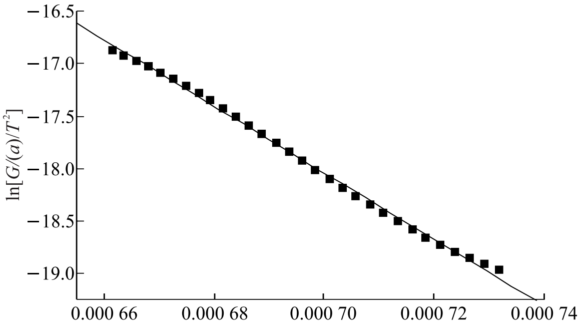

Fig.6 Carbothermal curve of ferrum niobate from 1 096 to 1 238 ℃

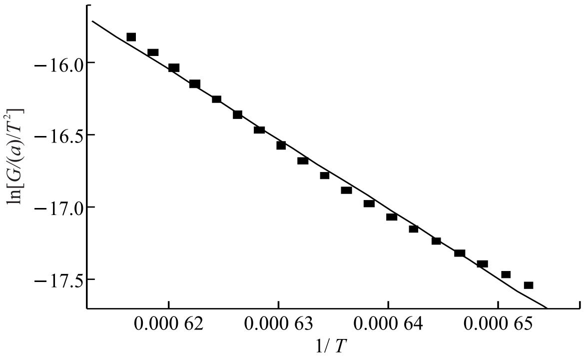

Fig.7 Carbothermal curve of ferrum niobate from 1 038 to 1 344 ℃

As is shown in Fig.4, the reduction of ferrum niobate to Fe and NbO_2 can be divided into two steps: the fitted curve from 1 000 to 1 096 ℃ is shown in Fig.5; the fitted curve from 1 096 to 1 238 ℃ is shown in Fig.6.And the fitted curve of NbO_2 reduced to NbC from 1 238 to 1 344 ℃ is shown in Fig.7. The kinetic calculation results of ferrum niobate carbothermal reduction reaction are shown in Table 2.

Generally, when a solid product layer is generated, the gas-solid reaction must go though the following three steps: external diffusion of gas reactants going though the gas boundary layer; internal diffusion of gas reactants going though the solid product layer to reach (or leave) the reaction interface; interfacial chemical reaction. A small amount of ferrum niobate ($FeNb_2O_6$) and adsorbed carbon are directly reduced to NbO_2,

Table 2 Kinetic parameters of ferrum niobate carbothermal process

Temperature range/℃	Kinetic mechanism function	Control step	Apparent activated energy/(kJ/mol)	Correlation coefficient
1000-1096	$[-\ln(1-a)]^4=kt$	Chemical reaction of random nucleation and subsequent growth	394.4	0.998 51
1096-238	$a+(1-a)\ln(1-a)=kt$	Two-dimensional valensi diffusion	264.4	0.998 77
1238-1344	$[(1-a)^{-1/3}-1]^2=kt$	Three-dimensional Z-L-T diffusion	482	0.998 74

Fe, and CO in the initial stage of the reaction from 1 000 to 1 096 ℃. The generation and growth of new phase are the control steps, meanwhile, the activation energy is large and the reaction rate is slow. According to the two-step theory of direct reduction, only trace CO exists in the system, $FeNb_2O_6$ will be immediately reduced and CO_2 will be generated, moreover, CO_2 and C can generate duple CO. When the temperature is above 1 096 ℃, the main reaction is the indirect reduction of $FeNb_2O_6$ by CO. At the moment, abundant $FeNb_2O_6$ is reduced to NbO_2 and Fe, and the product layer forms quickly, so the contact between CO and $FeNb_2O_6$ particles is hindered and CO diffusion in the product layer is influenced. Thus, the internal diffusion of CO going through the solid products layer is the control step, and the fitted model is two-dimension internal-diffusion control model. When the temperature is above 1 238 ℃, the thickness of the product layer continues to increase and the diffusion resistance of CO in the product layer becomes larger, so the fitted model can deduce three-dimension diffusion control. The value of apparent activation energy is very high and reaches 482 kJ/mol which is close to that of carbothermal reduction of chromite in the final stage[10].

4 Conclusions

a)The initial temperature of ferrum niobate carbothermal reduction is about 1 000 ℃.The reduction process can be divided into two steps: the main reduction products are NbO_2 and Fe from 1 000 to 1 238 ℃; the main reaction from 1 238 to 1 344 ℃ is the reduction of NbO_2 to NbC.

b) The carbothermal reduction process of ferrum niobate being reduced to Fe and NbO_2 can be divided into two temperature stages: the kinetic equation is $[-\ln(1-\alpha)]^4=kt$ and controlled by nucleation and growth from 1 000 to 1 096 ℃, and the apparent activation energy is 388 kJ/mol; the kinetic equation, is $\alpha+(1-\alpha)\ln(1-\alpha)=kt$ and controlled by the two-dimension diffusion from 1 096 to 1 238 ℃ and the apparent activation energy is 264.4 kJ/mol. The kinetic equation of NbO_2 being reduced to NbC is $[(1-\alpha)^{-1/3}-1]^2=kt$ and controlled by the three-dimension diffusion from 1 238 to 1 344 ℃, and its apparent activation energy is 482.7 kJ/mol.

References

[1] Yu Y F. The Research on Comprehensive Utilization of Rare Earth and Niobium Resources in BayanObo Ore Is of Great Significance [J]. *Rare Earth Information*, 2007 (8): 8-9

[2] Lin D L, Li C L, Wu H L. *Technological Breakthrough and Progress on BayanObo Special Ore Mining* [M]. Beijing: Metallurgical Industry Press, 2007

[3] He X C, Fan P, Yang T J. Research on Improving the Niobium Recovery of Blast Furnace Smelting Iron Ore Contained with Niobium [J]. *Hunan Metallurgy*, 1990 (4): 1-4

[4] He X C, Yang Y Y, Dong Y C. Research on the Process of Niobium Entering into Iron Phase in the Smelting Reduction Stage of Niobium-enriched Furnace Burden [J]. *Hunan Metallurgy*, 1994 (5): 8-12

[5] Shinichi Ito. Synthesis of Tantalum-niobium Minerals and Mineral Processing Properties [J]. *Foreign Rare Metals*, 1986 (2): 33-36

[6] E T Turkdogan. *Physical Chemistry of High Temperature Technology* [M]. New York: Academic Press, 1980

[7] Li Y Z. *Thermoanalysis* [M].Beijing: Tsinghua University Press, 1987

[8] Hu R Z, Shi Q Z. *Thermoanalysis Kinetics* [M]. Beijing: Science Press, 2001

[9] Guo H J. *Metallurgical Physical Chemistry Tutorial* [M]. Beijing: Metallurgical Industry Press, 2004

[10] Sanchez-ramos, S domenech-carbo, A Gimeno-Adelantado. Thermal Decomposition of Chromite Spinel with Chlorite Admixture [J]. *Thermochim. Acta*, 2008, 476(1):11-19