40 Year History of Metal Silicon Production in China

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Abstract

The production of metal silicon in China started in August, 1957, which has been 40 years. In this article, its history, characteristics technical situation and achievement are described, and it shows the authors' views on the future development of metal silicon production.

1. Introduction

The first producer of metal silicon in China is Metal Silicon Plant of Fushun Aluminum Smelter, which started to produce metal silicon in August, 1957. During the past 40 years, especially with the increasing of export volume since 1980's. At present, there are over 400 metal silicon producers in China. Of which the total output reaches 400,000 tpy, exceeding the production capacity of U. S. A, and China has been the biggest producer in the world. In this article, the history, characteristics, existing technique situation and achievement of the production of metal silicon in China are described, and the authors' views on the future development of metal silicon production are also shown.

2. History and features

China has extensive resources of quartz and silica with high silicon oxide content, which were found in most provinces and regions of China. For most deposits, the reserves are more than 1Mt and easy to mine because of their thick layer and compact structure without apparent fissures.

In many regions, the SiO_2 content of the mineral is more than 99%.

According to some reports, there are also a lot of coal resources in China, of which the geological reserves are more than 500 billion t, and 100 billion t canbe mined.

These resources are distributed in many provinces and regions, especially in Shanxi, Shaaxi, Inner Mongolia and Ningxia. Restricted by the transportation conditions it is difficult to transport all coal outside. Some coal with lower calorific value is suitable to generate power locally. Except the extensive mineral and coal resources, Chinese waterpower resource is the biggest in the world, the theoretical reserve is 680000 MW, of which 380000 MW can be developed.

Such extensive mineral and power resources provide advantageous conditions to the production of metal silicon.

2. 1 Construction and development of metal silicon producers

Before 1949, Yellow — sea Chemical Industry Research Institute made some study on the reduction of silicon oxide, but there was no industrial production at the time. After the foundation of P. R. C, with the assistance of the former Soviet Union's experts, the first metal silicon producer Metal Silicon Plant of Fushun Aluminum Smelter started to produce in August 1957. In the 1960's, some producers in Liaoning, Jiangsu provinces and Shanghai city began to produce metal silicon.

In the 1970's, other producers in southwest, northern — China and northwest also began to produce metal silicon one after another. By the end of the 1970's, There were nearly 20 producers in China, of which all products were used in China and could meet the domestic demand.

In the late 1970's, with carrying out the policy of reform and opening to the outside, China began to export metal silicon. Because of its extensive mineral and labor resources, lower environmental request and production cost, and good quality of the product, especially close to the major consumer Japan, export to Japan was very competitive. In the 1980's, China exported metal silicon to Japan, Australia, Singapore, U. S., the former Soviet Union, and so on,.The amount exported to Japan was 183t in 1980, 64225t in 1990 and 110885t in 1996.

From the end of 1970's to mid — 1989, the production of metal silicon increased largely with the increasing of the domestic demand and export volume. There were many new producers and electrical furnaces started up. According to the statistics in 1990, there were nearly 400 producers with more than 400silicon furnaces, the production capacity had increased by a factor of 20 since the 1970's. These producers were distributed all over China, in the fields of non—ferrous metal and steel metallurgy, chemical and mechanical industry and so on. After 1989, affected by the international political fast — changing situation, Chinese metal silicon producers suffered frustration and hitting. In March of 1990 and Feb. of 1991, EEC and American Department of Commerce announced respectively that they would impose the anti—dump tax to Chinese metal silicon, which restricted Chinese products to export to EEC and America. Although Japan did not impose anti-dump tax on Chinese metal silicon, the price was reduced largely (the lowest price was US $ 350/t less than the price importing from Europe). In this situation, most of Chinese producers were obliged to stop production or convert to produce other products. There were also some producers survived from the frustration and the competition, which became stronger in the changing market. Entering the 1990's, the actual operating producers were reduced to less than 150 from 300.

In the early 1990's, there were some electrical furnaces stopped or idled in either China or foreign countries as the widely reduced price. Until 1994, with the increasing of the consumption of metal silicon, the relation between supply and demand was changed. In the Western countries, the supply could not meet the demand. For example, in 1994, the consumption of the Westerns reached to 765000t, except their own output of 574000t and import of 17000t from the Eastern countries, there was still a shortage of 20100t. It was the change of relation between supply and demand that made the price of metal silicon increased largely from 1995 to mid — 1996. Till the first quarter of 1996, the export price of metallurgical silicon increased to US $ 1300/t from 780/t, which had great temptation to most of Chinese producers even though the price is still lower than the price of international market. As a result, in the late 1995, some idled producers re-started and some new electrical furnaces were constructed, Chinese metal silicon production was again in the tendency of quick development, the restarted and newly constructed electrical furnaces were nearly a hundred. However, after 1996, with the metal silicon price reduced again and the power price increased, some producers would be faced of difficulty and the actual operating rate of Chinese metal silicon producers would be reduced.

2. 2 **Achievement and features**

From 1957 to the end of 1970's, nearly 20 producers of metal silicon was constructed one after another. Since the end of the 1980's, another 300 producers have been constructed. For the above mentioned producers, most were constructed on basis of the existing conditions no matter how simple and crude they were, and some producers were converted from the producers of calcium carbide and ferro—silicon. Both the capacities of the electrical furnaces and the production scale are very small. In such case, it was easy and quick from raising fund to construction and to production, and the economic result could be gained quickly. For some producers, it only took half year from construction to production, and the total investment could be taken back after a year. These medium and small enterprises provided many opportunities of employment to Chinese people, and made the mineral resources fully used. As these enterprises were distributed all over the China, the

surplus power of remote regions and seasonal hydropower could be used.

By export their products, the income was increased. And it also pushed the development of local power industry.

Before the 1970's, Chinese silicon products could only meet the domestic demand. Since 1980's, the products not only had met the domestic demand but also had exported a large amount to foreign countries. From 1981 to 1990, China exported 370000t metal silicon to Japan, and 523000t from 1991 to 1996. Only in the year of 1994, China exported metal silicon 116000t to the Western countries. Until now, China has exported silicon to Japan, West Europe, North America, Southeast Asia and Egypt.

3. Technical situation and advantages

In 1957, there was only one set of electrical furnace with 5000KVA, double electrodes, single phase. After development of 40 years, there are nearly 400 sets electrical furnaces in China, including the electrical furnaces with single phase, double electrodes, and with three phases, three electrodes. During the 40 years, China metal silicon production has made great progress on the reductant used, product quality and mechanization, and done a lot of work on fume treatment and utilization. Comparing with advanced international level, either the capacity of Chinese electrical furnaces or its mechanization level is still lower, but some indexes of Chinese metal silicon producers such as power consumption and unit consumption of electrode have reached the international level or leading in the world. The two electrical furnaces exported to Romania and the quick increased export indicate that the technology of Chinese metal silicon production has been in the rather higher level. The technological development of Chinese metal silicon production could be divided into the following respects:

3. 1 Using various carbonaceous materials as reductant

In the late 1950's, at the beginning of metal silicon production, charcoal was used as main reductant, of which the unit consumption is over 1. 5t. In the mid —1960's, mixed reductant with charcoal, petroleum coke and bituminous began to be used. After the 1970's, some experiments on reductant were made, such as using corn cobs, wood lumps, and furfural residue instead of charcoal as reductant, using petroleum coke as reductant, and increasing the coal percentage in reductant, which obtained good result, and have been adopted by some producers.

China has extensive coal resource, some high-quality coal has been found in Shanxi province, Inner Mongolia and Ningxia regions, which are non sticky, with good activity, high specific resistance, lower ash content of 3—5%, and lower graphitizing degree at high temperatures. Metal silicon producers in Datong county, Shanxi province, and Wuhai city, Inner Mongolia region, fired the coal into "blue charcoal", and mixed it with charcoal and petroleum coke to produce a kind of reductant. Using this reductant, not only produced good quality silicon with the impurity content of Fe, Al and Ca less than 0. 3%, 0. 3%, and 0. 06% respectively, but also reduced the cost of reductant and metal silicon.

In China, there are some producers still using small electrical furnaces (less than 2500KVA), which can only produce small amount of liquid silicon per tap, which is disadvatageous for refining outside the furnace. In order to ensure the silicon quality without refining, some producers use only petroleum coke as reductant, which made the production stable and the impurity content of Fe, Al, and Ca less than 0. 5%, 0. 5%, and 0. 3% respectively.

Using charcoal, petroleum coke and bituminous coal, or charcoal, petroleum coke and wood lumps as mixing reductant, some metal silicon producers also have good results. For 5000KVA electrical furnace with single phase, double electrodes, to produce 1t metal silicon, when the consumption of charcoal, petroleum coke and bituminous coal are 1151kg, 266kg and 37kg respectively, the unit consumption of power and electrode are 11611kwh and 85kg respectively. For 6300 KVA electrical furnace with three phases, three electrodes to produce 1t metal silicon, when the consumption of charcoal, petroleum coke and wood lumps are 1154kg, 498kg and 46kg respectively, the unit consumption of power and electrode are 11101kwh

and 68kg respectively.

3. 2 Control and regulation of charge ratio

The medium and small producers with lower mechanized level control the charge ratio relying on careful operation and management. In the course of metal silicon production, one important thing is to select suitable electrical parameters and geometric parameters of the furnace, the other important thing is careful observation and operation. The material and charge ratio of materials should be regulated according to the actual condition of the furnace and change of moisture and lump size of the reductant to keep the lump size and charge ratio suitable. Under this condition, the charge of the furnace would have higher resistance coefficient, fewer silicon carbide formed and the electrode can be embedded deeply. Thus, higher working voltage can be applied to increase the output and decrease the power consumption. For example, using electrical furnaces with 1800KVA, working voltage of 90—93V and the distance of 300—350mm from electrodes' tip to the furnace bottom can be kept, the output can exceed 100t per month /furnace, and the unit consumption of power is not more than 12800kwh.

In order to reduce the impurity content of the reductant, some producers select qualified charcoal and wash it to eliminate the scrap of the charcoal and the parts of tree bark containing more calcium, and then the washed charcoal is directly fed into the furnace. As the washed charcoal contained some water, which can prevent the surface of charge from overheating and collect the SiO on the upper layer easily.

3. 3 Increasing the varieties and improving the quality of the product

Before the 1980's, most metal silicon produced by Chinese producers weremetallurgical grade silicon, which was refined by chlorinating method. Using this method, the impurity of Ca could be removed easily, but the impurity of Al could not be removed thoroughly and the environment was polluted seriously. The refined silicon is easy to absorb water, which affects the appearance of the product.

Since the 1980's, the consumption of chemical silicon on organosilicon and semi-conductors have increased quickly, the chemical silicon consumption of the Western countries had accounted for 42% of the total consumption of metal silicon till 1995.

Under normal condition, the price of chemical silicon is US $150 — 200 higher than the metallurgical silicon. Recently, many Chinese producers have realized that it is very important to develop the production of chemical silicon, and they have done a lot of work on organizing the production of chemical silicon and improving the quality of the products. Now, some producers have mastered the technology of oxidation method, which can overcome the disadvantages of chlorinating method, get good result on removing impurities Al and Ca, reducing the pollution and avoiding the product absorbing water, etc.

Now, some Chinese producers can produce metal silicon with high quality by means of chlorinaton or oxidation. The chemical silicon they produced have been sold in the international market, of which the content of impurity of Fe, Al, Ca are not more than 0. 2%, 0. 2% and 0. 02% respectively.

3. 4 Improvements on short bus and body of electrical furnace

Recently, some scholars and entrepreneurs made a lot of research on the structure and material of short bus and copper bushing of the electrical furnace and invented some patents. The invention " power saving device a new electrode holder of electrical furnace" was patented in June, 1990. In this patent, using a graphite bushing instead of copper bushing, which simplified the structure, saved copper, reduced the contacting resistance between contact bushing and electrode and power consumption. This technology has been used in some producers.

In general, the lining of electrical furnace is built of carbon bricks at the bottom, graphitized carbon bricks or baked carbon bricks on the side wall, and refractory clay bricks on other parts. Recently, using the experience of other field, self — baking bricks are used in the lining of electrical furnace, which are baked during drying and production. Such carbonaceous bricks are firm, and compact, which can avoid permeation of the liquid silicon. In this case, hot paste and ramming are not needed, which

also can improve the working conditions of construction and reduce the cost.
Unsuitable material and technique for the furnace hole often make the furnace leak, which affect the normal production. Recently, some producers use a new material with silicon carbide binded silicon nitride instead of alumina—containing brick as the material of furnace hole, which reduced the times of leakage.

3.5 Fume treatment and recovery

From 1970's to 1990's, ESP and bag filters were used to treat the fume emitted from the electrical furnaces of 2700KVA, 3200KVA, 5000KVA, 6300KVA, positive-pressured glass-fabric bag filters has been used in the electrical furnace of 2700KVA and 3200KVA for many years. Since 1990's, bag-filter with counter blowing has been used in the electrical furnace of 6300KVA and silicon oxide densifying equipment has been introduced. In order to make full use of the waste heat, some producers changed the open type furnace into short hood fume enclosure, and installed waste heat boiler, by which great achievement has been achieved on fume scrubbing and recovery.
After studying for many years, it is verified that the dust with high content of silicon oxide can be used in a concrete with high strength, and another concrete with high resistance to freezing and acid, which have been applied in many fields. Using this dust also can produce a heat insulating material, which can be used as the insulated layer in the aluminum electrolyzer cells.

4. Prospects for the coming century

After the development of 40 years, some key enterprises of Chinese metal silicon have made great progress and achievement. As for the medium and small enterprises, however, most of them need further improvement on technical management, and others should be forced to stop production or convert to produce other products according to the supply condition of power and materials.
Though the quality and varieties of Chinese metal silicon have great improvement, the output of chemical silicon is still lower. The urgent matter is to continue to improve the quality, output and export volume of chemical silicon.
For many years, restricted by the diameter of graphite electrode, the actual capacity of electrical furnace was limited within 6300KVA, which hindered the increasing of unit furnace output and reducing of various consumption indexes, and also is unfavorable to the fume treatment and the process automation.
In the future, the producers with good conditions should research and use electrical furnace with large capacity (more than 10000KVA), or use self-baking electrode or carbon electrode with big diameter. If possible, co-operate with carbon product enterprises to produce graphite electrode with big diameter. It is also important to co-operate with foreign countries to absorb foreign fund and introduce their advanced technology during solving the problems.

5. Conclusion

After 40 years development, Metal silicon production in China has made great progress on increasing the production capacity and export volume, and reducing the unit consumption of power and electrode, which attracted worldwide attention. However, comparing with the advanced countries, we still have a long way to go, especially on the capacity of electrical furnaces and automation. In order to serve the development of the world economy, Chinese metal silicon producers hope to co — operate with foreign countries to introduce their investment and technology to produce the product with high quality and low price.