POSTER

THE EFFECT OF COKE QUALITY IN THE PRODUCTION OF SiC

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1. INTRODUCTION

Historically the production of petroleum coke is focussed on two big areas: the manufacture of carbon anodes in the aluminium smelting cells and the production of electrographites for the steel industry [1]. Nowdays, the reduction of smelting cells and the crisis of the steel industry, is producing a continuous decrease in the consumption of coke. For this reason it is necessary to open new markets, specially in the area of non oxidic ceramics (i.e. SiC). Silicon carbide is commercially produced by reaction of high grade silica sand or quartz and carbon in an electric resistance furnace (Acheson's method). The carbon is in the form of petroleum green coke. Two different types of silicon carbide are available by this method (it depends on the purity of the raw material): black SiC (low purity) and green SiC (high purity). The black colour is produced by the aluminium impurities present in the silica sand.
Usually in the industry of SiC the requirements for the coke are not very restrictive: just a maximum in ash and sulphur content and a minimum in fixed carbon content. The aim of the present work is to demonstrate that it is necessary to know more properties of the coke for increasing the quality and productivity of SiC manufacture.

2. EXPERIMENTAL

Eleven different petroleum green cokes have been studied. Eight of them are used in the industrial production of SiC with different results. Standard techniques (elemental analysis, Fourier-Transform Infrared-absorption) were carried out to establish the quality of the different cokes. Optical texture of the cokes was assessed by reflected optical microscopy. Reactivity (oxidation resistance) tests were carried out in two ways: by using thermogravimetry analysis (TG) for the as-received coke and by using simultaneous thermogravimetry differential thermal analysis (TG-DTA) for the cokes previously heat treated at 900 °C for eliminating the volatile material. Oxidation resistance studies (1 atm.) air, 60 cm^3(STP)/min) were performed by both nonisothermal and isothermal analysis. The non isothermal analysis were carried out at a heating rate of 10 °C/min, and the isothermal at a temperature of 500 °C

3. RESULTS AND DISCUSSION

Table 1 shows the elemental analysis of the cokes. It can be seen that all the cokes have similar contents in carbon, volatile material, sulphur and ash, but the results in the SiC production are very different. Then, this classification method is not appropiate for selecting the coke for making SiC.
The infrared absorption spectra of the different cokes are very similar, only varyng the intensity of two significant bands. The most important band are: 3450 cm^{-1} (stretching vibrations of N-H bond), 3050 cm^{-1} (stretching vibrations of C-H bond in aromatic ring), 2960 cm^{-1} (asymmetric stretching vibrations of C-H bond in methyl groups), 2920 cm^{-1} (asymmetric stretching vibrations of C-H bond in methylene groups), 2860 cm^{-1} (symmetric stretching vibrations of C-H bond in methyl and methylene groups), 2720 cm^{-1} (stretching vibrations of C-H bond in the bridge structures ($CHAr_3$)).
The intensity ratio between the band at 3050 cm^{-1} and the band groups in the range of 2800-3000 cm^{-1} is representative of the ratio of aromatic/aliphatic groups that is closely related to the reactivity of the coke. The reactivity increases with the increment of aliphatic groups [2,3]. Table 2 shows the aromatic/aliphatic ratio. It is noted that the increase of aromatic content increases the resistance of coke to oxidation (see Table I); this is not a direct relation but only a tendency because the oxidation resistance not only depends on the structure of coke, but also on the impurities content, are very important (V, Fe, Ni are catalysts of the reaction).
The typical TG-DTA profile shows a double exothermic peak that corresponds to the combustion of the coke. Table I only shows the temperature of the bigger peak. A good relation can be observed between the peak temperature and the yield in the industrial process. This relation is very important because to our knowledge , no one has observed a relation between the usual parameter of the coke classification (sulphur content, volatil material, fixed carbon, ashes) and the yield in the SiC production.
Probably the doubled peak is produced by two combustion processes, the first one corresponding to the combustion of the most reactive coke (mosaic optical texture) and the second one to the combustion of the domain and flow domain of the coke [4-6]; this is supported by the observation of optical texture by optical microscopy, where the coke with a superior

content in domains and flow domains has a bigger second peak. Similar results are observed in the isothermal reaction with air at 500°C. The main difference between the two methods are: i) the information of non isothermal method is higher (i.e the two combustion process can not be observed in isothermal reaction) ii) the control of the affecting parameter in the non isothermal reaction is more difficult.

4. CONCLUSIONS

In this paper, we have presented experimental results that indicate that reactivity of coke is indirectly related with the quality and yield in the industrial synthesis of SiC. The usual parameters for determinating the coke quality (carbon content, ash,...) are not appropriate for selecting the coke for SiC manufacture. It is necessary to know and to control the optical texture and the chemical structure (content in aliphatic and aromatic groups) in order to select the coke, because these parameters are closely related with reactivity.

Acknowledgements

The authors would like to express their gratitude to Pablo Martínez of "NAVARRO, S.A." for the determination of the industrial results and for useful comments, suggestions and a critical reading of the manuscript.

5. REFERENCES

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Table 1 Analysis of different green petroleum cokes used in this work

Sample	Volatile (wt %)	Ash (wt %)	Fixed C (wt %)	Sulphur (wt %)	ATD-peak (°C)	Industrial result
1	9.76	1.14	89.10	6.21	650	Very Good
2	7.22	0.78	92.00	5.31	600	Bad
3	10.11	0.44	89.45	5.70	584	Bad
4@	6.64	0.12	93.24	1.40	689	Good
5	8.00	0.44	91.56	6.38	665	Med-Good
6@	8.52	0.21	91.27	1.54	698	Med-Good
7	9.43	0.62	89.25	3.83	655	Med-Good
8	9.53	0.37	90.10	4.03	603	not-used
9	8.9	0.45	90.65	4.85	595	Medium
Regular	9.95	0.15	93.76	1.09	702	not used
Combustion	12.34	0.30	87.44	6.05	590	not used

@ Utilized to make green SiC

Table 2 Ratio of aromatic/aliphatic groups, obtained by FTIR

Sample	1	2	3	4	5	6	7	8	9	Reg.	Com.
ratio aro/ali	1.3	0.9	0.9	1.4	1.2	1.3	1.2	1.0	0.9	1.2	0.9