

REACTIVITY OF ALUMINUM-DOPED BINDER COKES

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Introduction

AlF₃ and Al₂O₃ have been suggested as anode additives that may reduce the excess carbon consumption due to CO₂ and airburn reactions during aluminum electrolysis [1-3]. At the same time, others have indirectly pointed out that both aluminum metal and the oxide may have a weak catalytic effect on the gasification reactions [4,5]. However, industrial raw materials that contain a whole spectrum of impurities are used in many of these investigations. To avoid the disturbing and masking effect of these uncontrollable impurities, this work used cokes with defined contamination profiles, produced from high purity coke precursors in a special pressurized lab-scale coker.

Experimental

Three different series of aluminum-doped cokes were made; one to which different amounts of aluminum-acetylacetonate was added (the "Alac" series), one doped with aluminumacetylacetonate and 1 wt% sulfur ("SAlac", sulfur was added as dibenzothiophene) and one doped with aluminumfluoride ("AlF3"). A high purity aromatic oil was used as a precursor for the Alac- and SAlac cokes and a low-ash petroleum pitch for the AlF3 cokes. The doped precursors were carbonized in a pressurized lab-scale coke reactor at 525°C (heating rate 3°C min⁻¹). The green cokes were baked to a maximum temperature of 1010°C for 2 hours. The calcined cokes were crushed and a -2+1 mm fraction was screened out for reactivity testing.

The gas reactivity measurements were performed using a thermobalance equipment manufactured by Hydro Aluminium, Norway. The reaction temperature was 525°C for the air reactivity tests and 960°C for the CO₂ tests. The results were reported as milligram gasification loss per hour and gram coke [mg/g h]. The coke textures were expressed in terms of mosaic- and fiber indexes using a polarizing light microscope and an automatic image analysis program (see [6] for further descriptions).

Results and Discussion

EDX-analysis indicated that the aluminumacetylacetonate predominantly decomposed to Al₂O₃ during the

carbonization and baking process. Figure 1 and 2 shows the reactivities of the Alac- and SAlac cokes versus the analyzed aluminum content. According to these figures, aluminumoxide act as a relatively strong catalyst towards both the air and CO₂ gasification reactions.

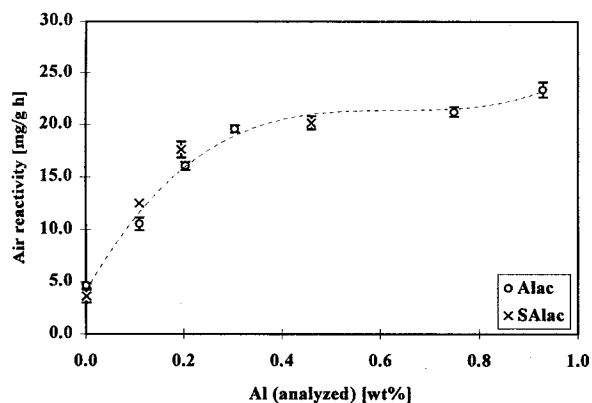


Fig. 1 Air reactivity of Alac- and SAlac cokes

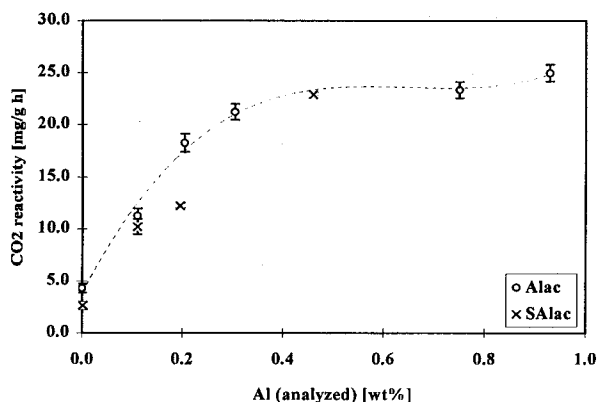


Fig. 2 CO₂ reactivity of Alac- and SAlac cokes

However, the texture analysis revealed that the additions of aluminumacetylacetonate interfered with the growth and coalescence of the mesophase particles during the carbonization process. The intrinsic reactivity is expected to depend on the coke texture since a fine mosaic texture (high mosaic index) gives more active sites for the gasification reactions than a coarse texture. Thus, the overall coke reactivity should be expressed as a function of both the aluminum content and the mosaic index, as shown for the air reactivity in Figure 3.

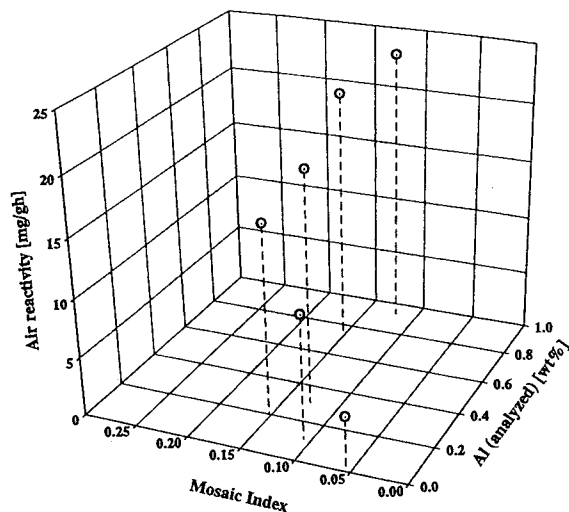


Fig. 3 Air reactivity of Alac cokes vs. Al-content and mosaic index

The extra sulfur addition has no statistically significant effect on neither the air nor the CO₂ reactivity. Hume *et al.* [7] found that sulfur inhibited the sodium catalysis of the carbon-CO₂ reaction by forming a stable non-mobile complex with sodium. In this work, it was believed that sulfur could cause a similar reactivity reduction by e.g. forming a comparable complex with the aluminumoxide. However, due to the addition of dibenzothiophene, the mosaic texture of the SAlac cokes was finer than for the corresponding Alac cokes. This may explain why the coke reactivities weren't reduced.

The aluminum particles on the surface of the calcined AlF₃-cokes consisted of an Al-C-O phase. Only a few of the analyzed particles contained minor amounts of fluorine. Figure 4 and 5 shows the measured air and carboxy reactivities versus the analyzed aluminum content. The aluminumfluoride additions seem to lower the coke reactivity towards both the carboxy and airburn reactions. The results correspond well with those reported by Sørli *et al.* [1]. However, it remains to be clarified by which mechanism the AlF₃-addition inhibits the carbon-gas reactions. SEM-studies of reacted coke samples indicated that the aluminum-containing particles were catalytically active during the gasification reactions. According to Braunschweig *et al.* [2], aluminumfluoride vapor evolved at temperatures above 900°C reduces the activity of AlF₃-doped anode carbon. The EDX-analysis indicated that considerable amounts of volatile fluorine compounds had been given off the particles during the carbonization and baking process. Sulfur was enriched in the aluminum particles during the reactivity measurements. The additions of various amounts of aluminumfluoride did not have any apparent influence on the carbonization process and the

resulting coke texture. The observed reactivity behavior may therefore be due to a combined effect of both fluorine-deactivation of the intrinsically active sites by e.g. adsorption and sulfur poisoning of the catalytically active aluminum particles.

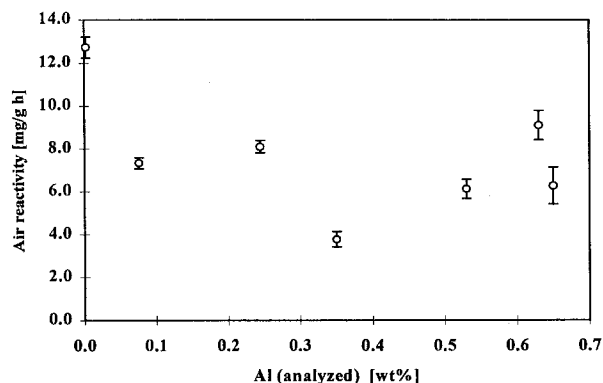


Fig. 4 Air reactivity of AlF₃-doped cokes

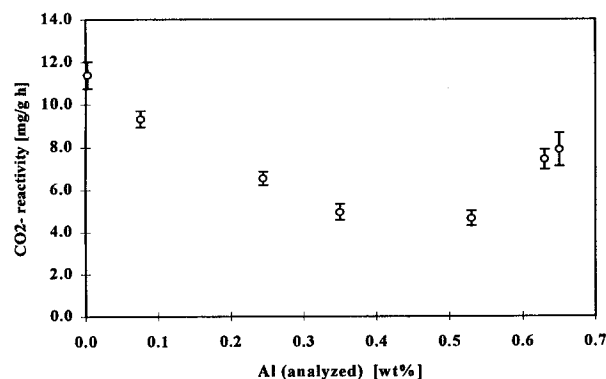


Fig. 5 CO₂ reactivity of AlF₃-doped cokes

Acknowledgments

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References

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