EFFECTS OF SULPHUR, NICKEL AND VANADIUM
ON THE AIR AND CO₂ REACTIVITY OF COKES

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Introduction

Carbon anodes represent a major production cost in the primary production of aluminum. Approximately 400-450 kg net anode carbon is consumed per ton aluminum produced. The theoretical need is 334 kg C / t Al. Apart from carbon dust formation, excess carbon consumption is caused by the oxidation of the anodes by air and CO_2 under evolution of CO_2 and CO. These reactions which may cause an extra carbon consumption of 20 to 150 kg C/ t Al [1], are catalyzed by many different inorganic impurities present in the carbon anode materials. This work is an investigation of the effects of sulphur, nickel and vanadium on the reactivity of anode cokes, and it is a continuation of our work on the effects of iron [2,3].

Experimental

Coke preparation

To avoid the uncertainties that are introduced by the often complex background impurity content in anode grade petroleum cokes, a laboratory coker able to produce green cokes with controlled impurity levels has been developed [3]. With this apparatus one can design cokes with known composition. This was done by using an aromatic oil from the distillation of coal tar pitch as the coke precursor, adding controlled amounts of inorganic impurities. Nickel was added to the precursor as nickel-(II)acetylacetonate, vanadium as vanadium(III)acetyl-acetonate and sulphur was added as dibenzothiophene. The coke precursors were heat-treated to 525 °C in the coker under 15 bar argon pressure.

The green coke was crushed in a jaw crusher to - 10 mm grain size after coking, and then calcined to 1000 °C.

Gas reactivity of carbon materials

In this study the Hydro Aluminium air/CO_2 reactivity apparatus was used to measure the gas reactivity of the cokes. The standard reaction temperatures for this equipment are 525 °C in air, and 960 °C in CO_2. To investigate the reactivity of cokes, 10 g samples of grains in the size range 1 - 2 mm are used. The weight loss due to gasification is recorded continuously at constant temperature and with excess reaction gas, and the weight loss rate, r ([mg/h]), is calculated. The gas reactivity, R_g, (based on sample mass, not apparent surface area) is given by:

Gas reactivity [mg/g h]:

$$R_g = \frac{r}{m_0} \qquad (3)$$

where m_0 is the original weight of sample [g] and r is the weight loss rate [mg/h].

Results and Discussion

Sulphur

Six cokes were made with different S levels. As shown in [3], approximately half of the added sulphur was fixated in the coke after calcining. Apparently, sulphur alone did not have any large effect on air and CO_2 reactivity in the concentration range between 0.35 and 1.8 wt%, as shown in fig. 1.
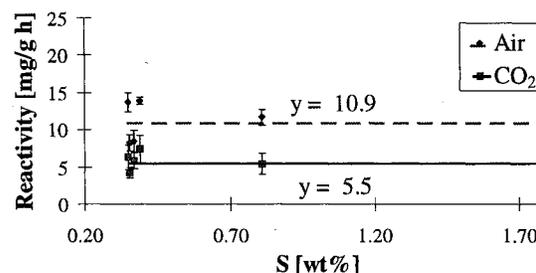

Figure 1. Air (525 °C) and carboxy (960 °C) reactivity of coke vs. sulphur content.
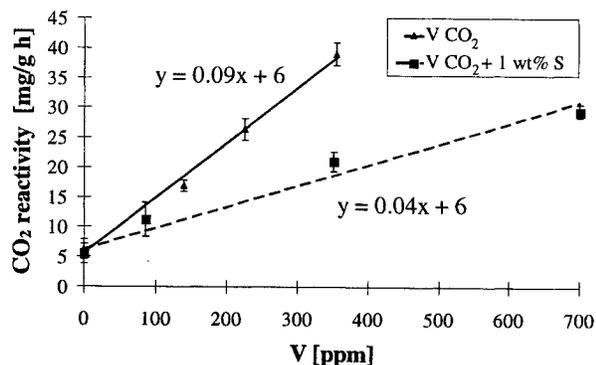
Vanadium

Vanadium is known as a very strong air burn catalyst of carbon anodes. It is also a strong carboxy reaction catalyst [4].

Different vanadium contents were added to four coke precursors (0, 100, 400 and 1000 ppm). The resulting calcined cokes contained 5, 140, 225 and 355 ppm vanadium respectively. Fig. 2 shows the carboxy reactivity of the cokes vs. the vanadium content.

To investigate the effect of sulphur on catalysis by vanadium, four cokes corresponding to the ones above were produced. 1 wt% sulphur was added to the precursors in addition to vanadium (0, 100, 400 and 1000 ppm). The resulting calcined cokes contained 5, 85, 350 and 700 ppm vanadium respectively. The sulphur content of the high sulphur cokes was 0.85 wt%, while the low sulphur cokes contained 0.35 wt% S. The carboxy reactivity of the high sulphur cokes is shown in fig. 2.

The carboxy reactivity increased with vanadium content, i.e. vanadium catalyzed the reaction. An increased sulphur level in the cokes reduced the effect of vanadium. Both the absolute reactivity value and the slope were decreased by sulphur addition.

The air reactivity of the cokes was too high to give reliable measurements with this reactivity apparatus even at the lowest possible reaction temperature (475 °C). Thus, vanadium is an extremely strong catalyst to air burn, and if sulphur inhibited the reaction, the effect was not sufficiently large to lower the reactivity into the measurable region.
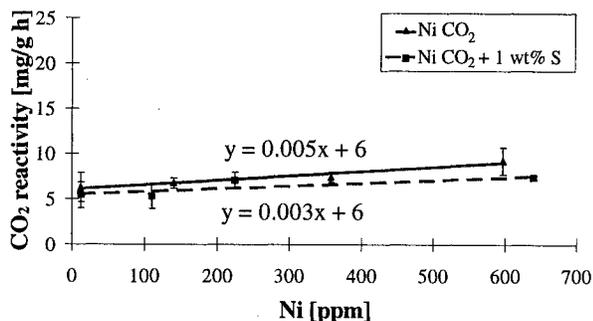
Figure 2. Carboxy reactivity of coke aggregate at 960 °C as a function of the vanadium content; cokes with and without 1 wt% sulphur added.

Nickel

Nickel has been reported to be a catalyst to both the air and carboxy oxidation of coke [4].

As with vanadium, different nickel contents were added to four coke precursors (0, 100, 400 and 1000 ppm). The resulting calcined cokes contained 10, 140, 360 and 600 ppm nickel respectively

To investigate the effect of sulphur on catalysis by nickel, four precursors with 1 wt% sulphur added were produced. The resulting calcined cokes contained 10, 110, 225 and 640 ppm nickel respectively. The high sulphur cokes contained 0.88 wt% S, while the low sulphur cokes contained 0.35 wt% S. Fig. 3 shows the carboxy reactivity of the cokes vs. the nickel content.
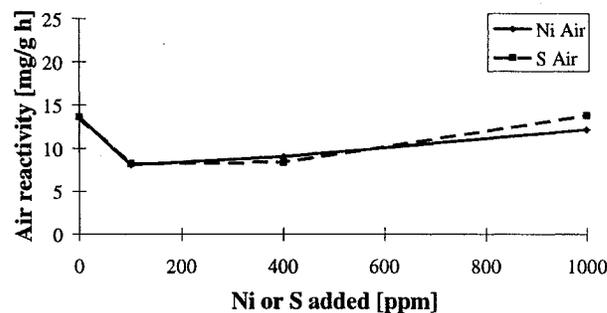

Figure 3. Carboxy reactivity of coke aggregate at 960 °C as a function of the nickel content; cokes with and without 1 wt% sulphur added.

Nickel did not have any great effect on carboxy reactivity. A small increase in reactivity with increasing nickel content is observed. Addition of sulphur caused a minor reduction in reactivity, but for most cokes the reduction was smaller than the standard deviation of the individual measurements.

The air reactivity of the cokes is shown in fig. 4. It seems like the air reactivity as a function of nickel content goes through a minimum. However, it is more likely that the minimum in reactivity is an effect caused by the organic part of the added nickel compound. This was seen when the air reactivity of the cokes with sulphur and nickel additives was plotted versus amount of substance added, fig. 5. The two curves superimpose.
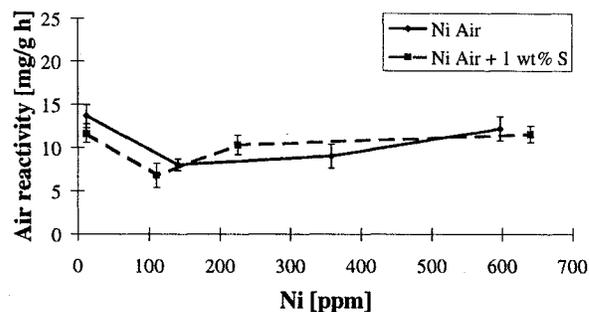
Figure 4. Air reactivity of coke aggregate at 525 °C as a function of the nickel content; cokes with and without 1 wt% sulphur added.

Figure 5. Air reactivity of coke aggregate at 525 °C as a function of the content of additives.

Conclusions

For anode cokes, sulphur alone did not have any large effect on air and CO_2 reactivity in the concentration range between 0.35 and 1.8 wt%.

Vanadium is a strong catalyst to both the air and carboxy reactivity of cokes. Sulphur inhibited the effect of vanadium on carboxy reactivity.

Nickel did not have any substantial effect on air and carboxy reactivity. Addition of sulphur caused a minor reduction in reactivity as a function of nickel content.

Acknowledgments

References

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