

The Reaction of Potassium and Potassium Salts with Carbons of Different HTT and Structure

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Abstract. This study examines at several reaction temperatures the interactions between potassium vapour and graphitizable and non-graphitizable carbons with a wide range of optical textures and heat treatment temperatures, under vacuum, nitrogen and carbon dioxide. Although the formation of intercalation compounds with graphitic carbon is established, the mechanism of carbon comminution by potassium vapour is not understood. Degradation of carbon of smallest optical texture occurs preferentially probably as a result of mixed staging of intercalates creating non-uniform stresses leading to macro-crack formation and degradation.

Introduction

This study is concerned with current understanding of the mechanisms of interaction/intercalation of potassium with graphitic, graphitizable and non-graphitizable carbons. There is industrial relevance in terms of interactions of alkali metal vapour with metallurgical cokes in the blast furnace and with carbon anodes and cathodes employed in aluminium production, these interactions causing significant degradation or comminution of the carbon artefact.

The formation of intercalation 'compounds' with single crystal graphite and their characterisation is well-established (1, 2). There exists a scattered literature describing interactions of potassium with the graphitizable (but non-graphitic) and non-graphitizable carbons. This literature has been critically assessed and reviewed (3).

Potassium forms intercalation "compounds" with graphitic carbons at $\sim 300^\circ\text{C}$ under vacuum or nitrogen associated with characteristic colour changes of the several stages. Potassium can intercalate with graphitizable carbons of $\text{HTT} > 1000^\circ\text{C}$ under vacuum/nitrogen at reaction temperatures $< 500^\circ\text{C}$. Extents of intercalation increase with increasing HTT of the carbon. No intercalates form with graphitizable carbons of $\text{HTT } 800^\circ\text{C}$. Mixed staging is characteristic of graphitizable carbons of $\text{HTT } 1500^\circ\text{C}$. A carbon dioxide atmosphere prohibits the formation of intercalates below $\sim 1100\text{ K}$ (4). Schlögl and Boehm (5) comment on the instability of graphite intercalation compounds. Potassium intercalates with non-graphitic carbons have been proposed. However, the evidence is not conclusive. Adsorption effects, within any microporosity of these carbons, causing swelling and fragmentation of carbon cannot be ruled out (6). Overall, little of the available literature is directly comparable. The heterogeneity of coals/pitches and their different treatments provide a wide variety of graphitizable carbons. There is little information describing the variations of

stabilities of intercalates with temperature in the presence of potassium vapour as distinct from stability under vacuum or under an inert gas. The stability of potassium incorporation (intercalation?) at elevated temperatures ($\sim 800\text{--}1200^\circ\text{C}$) in graphitizable, non-graphitic carbons appears to be higher than stabilities of incorporation by graphitic carbons. Hawkins et al. (7) studied the reaction of potassium vapour with nitrogen or carbon monoxide, with petroleum and metallurgical cokes, anthracite carbons and graphites at reaction temperatures $572\text{--}1200^\circ\text{C}$. In terms of carbon comminution, this was most severe at the lower reaction temperatures, the graphitic carbons exhibiting maximum resistance to comminution. Lu et al. (8) reported that extents of 'intercalation' of potassium into metallurgical cokes decreased with increased size of optical texture, i.e. a measure of anisotropy or graphitizability of the cokes. Reaction of potassium, under nitrogen at $300\text{--}600^\circ\text{C}$, led to comminution of the coke. Cokes of small optical texture (isotropic according to Lu et al. (8)) exhibited more fissuring than the graphitizable components of the cokes. The assessment of the literature (3) suggests that for the graphitizable carbons, potassium probably enters into the carbon structure via the electron transfer reaction associated with graphite. However, because these carbons are inherently less structured than graphite, the identification of staging of specific intercalation compounds (if intercalation exists as such) cannot be found. The presence of porosity within the non-graphitizable carbons facilitates interactions of surfaces with potassium which may enter into the less crystalline structure of such carbons, so producing swelling. Such swelling/expansion within the complex optical texture of cokes may produce the internal stresses and comminution of such coke pieces.

The objectives of this study are to examine extents of degradation/comminution by potassium vapour at different reaction temperatures of graphitizable carbons with a range of size of optical texture, and HTT to relate these parameters and to establish a

mechanism for the process of comminution.

Materials Used. Five metallurgical cokes, as obtained and HTT 1500, 2000, 2400, 2800°C were prepared together with a nuclear grade moderator graphite (HTT ~3000°C), a needle-coke (HTT ~1200°C) an isotropic coal char (NCB CR 901), (HTT 1100°C) and a natural flake graphite.

Experimental. These materials were reacted at 570°C to 910°C in sealed tubes, with potassium under vacuum and nitrogen-oxygen mixtures. The cokes and graphites were reacted with potassium vapour (from the metal) at 800°C in an autoclave under nitrogen. Similarly, the metallurgical cokes were reacted with potassium vapour from KOH at 910°C. Also, the metallurgical cokes were reacted with potassium vapour generated from a heated mixture of potassium carbonate and carbon black, at 910°C, both in an atmosphere of nitrogen and of carbon dioxide. The metallurgical cokes were also heated with liquid potassium at 70°C.

The cokes after reaction were monitored for physical appearance, optical texture was assessed by optical microscopy, the extents of comminution were monitored by scanning electron microscopy (SEM) and EDAX indicated extents of diffusion of potassium into the coke structures. Microstrength measurements indicated how coke structures may have been weakened following interaction/intercalation with the potassium vapour. The weakening of coke structure occurred via the formation of cracks within the coke as seen in Figures 1-3 for cokes from a semi-anthracite, a coking and caking coal respectively after reaction with potassium vapour at 910°C.

Conclusions. 1. After reaction with potassium from K_2CO_3+C , cokes from the higher rank coals (204, 301a) were consistently less degraded than those from the lower rank coals (401, 502). The optical textures most resistant to degradation were the single component structures, flow-anisotropy and isotropic. The multi-component mosaic textures were least resistant. 2. Heat treatment of metallurgical cokes increased their resistance by potassium vapour at 800°C under nitrogen. 3. Studies of the reaction of metallurgical cokes with potassium vapour at 70°, 570°, 800° and 910°C indicated that degradation occurred at all these temperatures. Maximum degradation occurred at 400°C for one system. 4. Degradation only occurred with reaction carried out under

nitrogen or vacuum. The presence of carbon dioxide prevented interactions. 5. The graphites and needle-cokes formed intercalates when the reaction temperature was 800°C under nitrogen. No reaction could be detected with the isotropic coal char. 6. Degradation of coke is thought to be due to mixed staging of intercalates with resultant non-uniform concentrations of potassium and high stresses leading to macro-crack formation and degradation.

References

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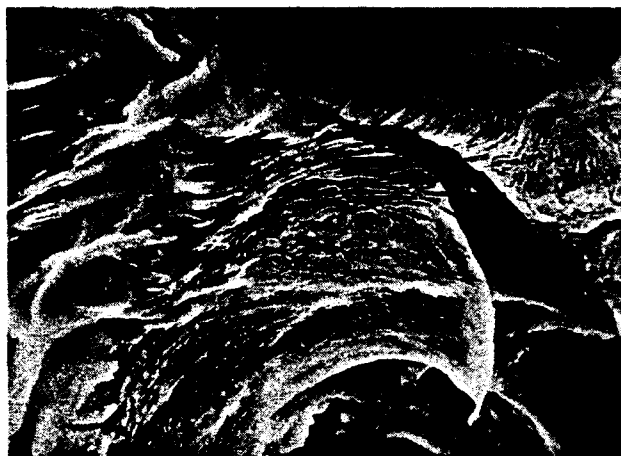


Figure 2. SEM Caking coal plus K.

15 μm

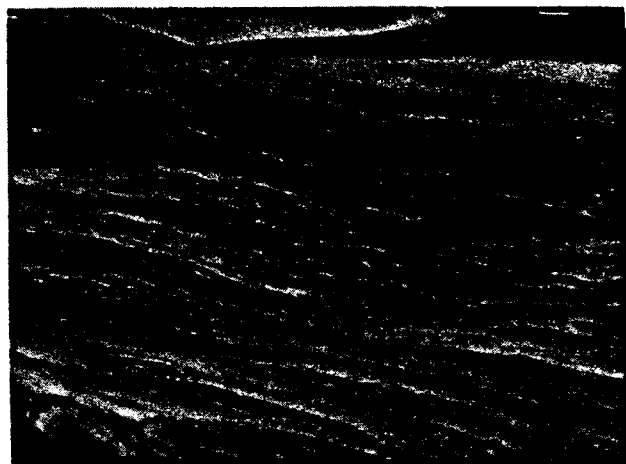


Figure 1. SEM Semi-anthracite coke plus K. 2 μm



Figure 3. SEM Coking coal plus K.

4 μm