

**A REVIEW OF THE CATALYTIC OXIDATION OF CARBON-CARBON
COMPOSITE AIRCRAFT BRAKES**

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Abstract

The use of de-icing chemicals at airport runways has been shown to produce oxides and carbonates of sodium, potassium and calcium which catalyse the oxidation of carbon-carbon composite aircraft brakes leading to an increase of the oxidation rate by an order of magnitude. This review reports on studies that have characterised the catalytic oxidation and discusses the mechanism of the catalytic reaction based on investigations that were carried out with both C-C composites and carbon as a fossil fuel. The alkali metal oxides/carbonates are more active catalysts and in their case, the redox reaction between the monoxides and the peroxides has been identified as the most likely catalysis mechanism. In order to reduce or eliminate the problem of catalysis, doping with boron or phosphorus compounds has been investigated by a number of researchers. The effect of these along with the use of protective coatings is also reviewed.

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1. Introduction

Carbon-carbon composites have found use as friction materials in the aerospace industry and in motorsport and are candidate materials for structural applications at temperatures in excess of 2000°C. A typical C-C composite application where friction properties are important is the use of these materials as friction brakes in aircraft. Following their introduction to aircraft in the 1970s [1], the function of C-C brakes has been (i) to decelerate and stop aircraft after landing by transforming kinetic energy into heat via friction and (ii) to dissipate away the resulting heat. In addition, aircraft brakes must be able to efficiently stop an aircraft during an aborted take-off. The reasons that have led to the use of C-C composites for aircraft braking applications in place of steel brakes include the ability of the former to maintain a stable coefficient of friction and to dissipate heat while maintaining dimensional stability at high temperatures (by having a lower coefficient of thermal expansion than steel). Other factors including the absence of fatigue problems and the low density of carbon (about three times less dense than steel) are also important. By combining the lower density advantage with the higher specific heat capacity of carbon over steel, a 60% weight saving is achieved for a similar brake temperature-operating range [1]. In real terms, this corresponds to about 500kg for each commercial aircraft [2]. Compared to steel, C-C discs are more cost-effective and can deliver an average of about 3000 landings, a figure which is about twice as high as that achieved with steel brakes [3]. In commercial aircraft, the high braking demand requires the sliding interface areas to dissipate approximately $450 \text{ kJ}\cdot\text{mm}^{-2}$ of kinetic energy per unit area to heat in about 30 seconds [1]. This can lead to high levels of heat generation which has been reported to result in temperatures around 1000°C [3] and up to 1400°C particularly during an aborted take-off [4]. At such high temperatures, the C-C brakes can suffer oxidation and therefore, the lifetime of aircraft brakes is dependent on the rate of oxidation. Thanks to the fast dissipation of heat by the C-C composites and the effective anti-oxidation measures taken by aircraft-brake manufacturers, initially there was little cause for concern. However, the introduction of alkali-based runway de-icing chemicals in the 1990s in place of the traditional urea- and glycol-based de-icers resulted in a drastic increase in the rate of oxidation of carbon-carbon brakes through catalysis of the oxidation reaction. The aim of this paper is to review the research work that has been conducted to date on the catalytic oxidation of C-C composites in the presence of acetates and/or alkali and alkaline earth metal oxides/carbonates. In addressing the mechanism of catalysis, some relevant studies that were conducted using solely carbon powder (rather than fibres or composite material) for

gasification are also reviewed. Finally some of the proposed mechanisms to reduce or eliminate the catalytic -effect are reviewed.

1.1 C-C composite brake manufacture

The microstructure of a typical C-C brake is presented in fig. 1 which shows the presence of carbon fibres embedded within a carbon matrix. The manufacture of carbon fibres has been reported extensively in the past [5, 6]; carbon fibres can be made from different precursors including pitch, rayon and polyacrylonitrile (PAN). In the case of C-C brakes, PAN fibres are needled together in three directions to form a cloth which then undergoes carbonization in an inert atmosphere. The carbonized cloth is then cut to a specific mould and several layers are laid on top of each other to form a carbon pre-form disc with a specified weight for production for a specific type aircraft. Several discs are compressed onto a jig and loaded into a predetermined position in a furnace which is heated inductively to about 1000°C. Natural gas is then introduced which infiltrates the disc preforms and deposits carbon in the gaps between the carbon fibres. The discs go through multiple infiltration cycles until target density is achieved. The discs are finally machined to the desired size using computer-controlled equipment.

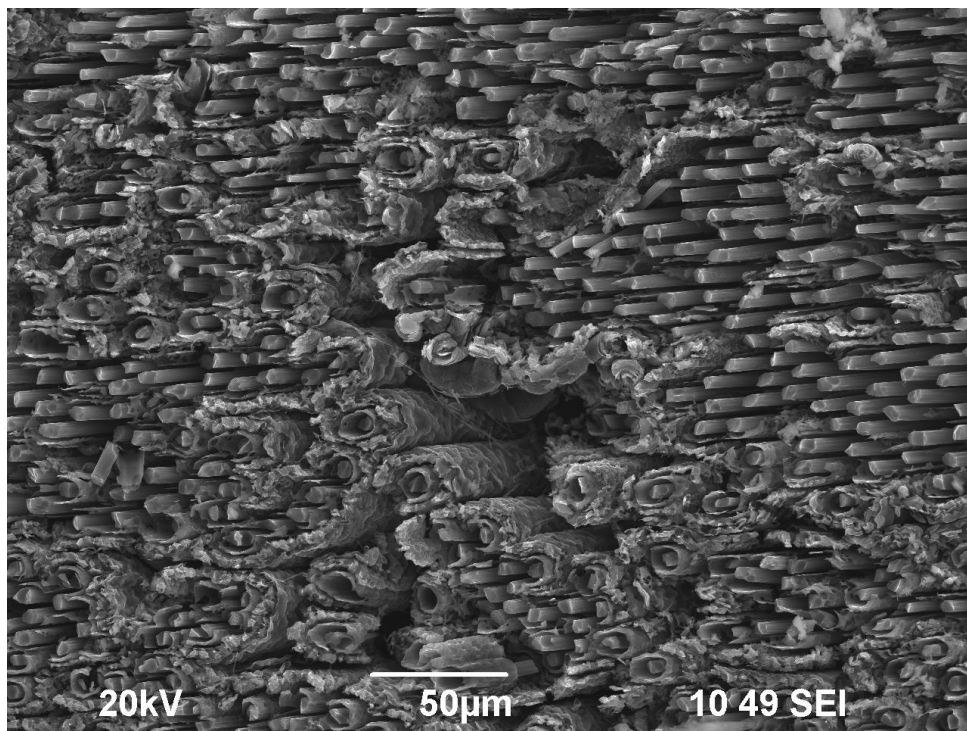


Fig. 1 SEM micrograph of a partially oxidised C-C composite showing carbon fibres in a matrix of carbon.

1.2 De-icing chemicals and their application

The use of de-icing chemicals has become essential in order to maintain safe-operating conditions both in-flight and at airport runways. The formation of ice on the aerodynamic surface of an aeroplane can affect in-flight handling, while icy runways are hazardous to aircraft as ice reduces the friction coefficient significantly and the aircraft tyres cannot ‘grip’ the runway surface. Anti-icing fluids are therefore sprayed directly onto aircraft to prevent ice formation, while de-icing chemicals are used to remove ice from runways. Traditionally these products were made from glycol and urea; while glycol products are still being used for aircraft deicing, the runway deicing fluids (based on urea) were substituted by alkali metal formates and acetates during the 1990s owing to the high aquatic toxicity and high values of both biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of urea. The COD value for urea de-icer has been reported to be 2.1 kg O₂/kg compared to 0.7 and 0.3 kg O₂/kg of de-icer for sodium and potassium acetates respectively [7]. While the introduction of the new de-icers led to improvements to the operational and environmental quality of winter maintenance activities at airports, several reports began to emerge highlighting some unexpected detrimental effects that included the catalytic oxidation of C-C brakes, cadmium coating corrosion, corrosion of airfield electrical and ground support equipment as well as degradation of asphalt and concrete [8]. Concerns arising from such observations led to the establishment of the Airport Cooperative Research Programme (ACRP) which collected and reviewed data on the damage caused by the new de-icers. According to the findings of the programme as summarised by Friedman et al [8], analysis of C-C brakes that were returned for service in the winter months indicated that brakes from aircraft operating in northern Europe had suffered more oxidation compared to those used in aircraft around the Mediterranean area. In addition, the brakes that came from aircraft operating in northern Europe displayed greater contamination from potassium as a result of the more extensive use of de-icing chemicals. Effectively, the catalytic oxidation of C-C brakes was the culprit. It was also reported that even cooler parts of the brakes were suffering from catalytic oxidation. At the temperature levels that develop as a result of friction, the sodium, potassium and calcium acetates and formates from the deicers decompose to the equivalent carbonates or oxides which are well-known for their catalytic effects on carbon-based reactions.

2. Catalytic oxidation of C-C composites; kinetics and mechanism of catalysis

C-C composite discs in aircraft have been reported to reach temperatures around 1000°C [3] during normal landing operations and up to 1400°C in extreme cases such as an aborted take-off [4]. Exposure to such high temperatures leads to thermal oxidation which is reported to be the main cause of degradation of C-C composites [8]. Whilst material loss occurs as a result of friction, according to Chang and Rusnak [9], at least 60% of the total weight loss is due to thermal oxidation. In another study by Chang [10] on the correlation between wear and oxidation of C-C composites, good agreement has been reported between the activation energy for the oxidation of carbon (122kJ mol⁻¹) and for material loss due to wear on non-frictional surfaces (113kJ mol⁻¹). Thus it was proposed that the mechanism of the wear loss is due to oxidation. In addition to the oxidation of the carbon matrix and fibres, this process also attacks the fibre-matrix interface and weakens the overall integrity of the composite [11]. As with graphite, C-C composites are thought to start oxidising at a temperature of around 400°C [12]. Oxidation becomes progressively more severe with further temperature increase [11]. As can be expected, studies on the kinetics of the oxidation of graphite, coal and coke (as fossil fuel materials) have been conducted extensively in the past. The problem of C-C composite oxidation is also beginning to attract attention owing to the problems that are being addressed by the aerospace industry. The potential use of this type of material in alternative high-temperature applications is likely to yield even more investigations in the future. A comprehensive study of the kinetics of the oxidation of C-C composites is indeed a complex task due to the various forms in which such a material can be manufactured and due to the variation in the resulting microstructure.

The oxidation of carbon can lead to formation of CO and CO₂ and mixtures of these and is summarized by the following reactions:



In the presence of water (in the form of steam), additional reactions as shown below may occur:





The use by the present authors of chemical thermodynamic data as compiled by Turkdogan [13], has shown that reactions 3 and 4 are possible only at temperatures above 667°C and 623°C respectively. As suggested by Savage [14] these reactions are probably not relevant for the case of C-C composite brakes as they are typically used in air and not in steam; moreover, the frictional heat is thought to lead to evaporation of any water that may be present. However, according to Blanco [3], the presence of adsorbed water within the C-C composite structure can be highly detrimental as it can enhance the polarity of active sites that contribute to carbon degradation during oxidation. This observation was further supported by evidence presented by Duvivier et al [15] who investigated the effect of 5% water vapour in air on the oxidation of C-C composite disc samples in the presence of K_2CO_3 catalyst at temperatures between 500°C and 650°C. Their results showed that the presence of water vapour could enhance the kinetics of oxidation by an order of magnitude.

The oxidation of carbon is characterised by several intermediate reactions. Some oxygen atoms are not immediately oxidised and remain bonded to the carbon surface in a variety of ways, partaking to the attempt of the carbonaceous surface to anneal the defects caused by the removal of carbon atoms by the oxygen. Carbon monoxide and dioxide are then formed via a sequence of reactions involving mobile surface oxygen complexes at active sites [3]. According to Bacos [16], the oxidation of carbon unfolds according to the following steps:

1. Oxygen diffusion through the boundary layer.
2. Oxygen diffusion through the cracks and pores of the carbonaceous surface.
3. Chemical reaction between carbon and oxygen and formation of oxidation products.
4. Gaseous product diffusion through the cracks and pores of the carbonaceous surface.
5. Gaseous diffusion of the products through the boundary layer.

Since it involves gaseous products and reactants, the oxidation reaction rate is expected to be influenced by both pressure and temperature conditions. Different levels of temperature and pressure can determine which of the five steps presented above becomes rate-limiting. Using a series of micrographs, Bacos [16] has shown that at low temperatures, the slowest and thus rate-determining step is the chemical reaction between carbon and oxygen, while the fastest step is the oxygen and product diffusion through the boundary layer. However, the temperature where the change in the mechanism took place is not given in that investigation.

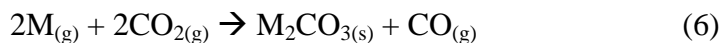
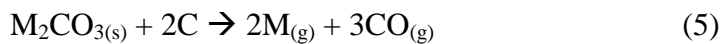
In fact, no kinetic data were presented either and these deductions on the rate-controlling mechanisms were based entirely on observations using sectioned samples. At low temperatures, it was shown that the oxidation process occurs mainly within the bulk of the material. Two types of porosity were identified; (i) transverse cracks and fibre-matrix de-bonding both of which contributed mainly to mass transport and (ii) pores within fibre bundles affecting mainly the chemical reaction. The oxygen molecules are able to penetrate into the pores of the material and they facilitate the formation of crevices within the bulk. These crevices then become longitudinal channels reducing the bulk to a highly porous skeleton where effectively only the fibre reinforcement remains. This observation implies that at low oxidation temperatures there is little or no shrinkage of the composite until the latter parts of oxidation. At high temperatures, the slowest step has been reported to be the oxygen diffusion through the boundary layer and the fastest is the chemical reaction. Additional support for this observation has been provided by Yasuda et al [17] who reported that the rate-controlling step changes from chemical reaction-control to diffusion-control of the gaseous species through the boundary layer at higher temperatures. Kinetic data presented by these authors [17] showed that as the temperature of oxidation increased, the relationship between weight loss with time changed from linear to parabolic at temperatures between 662°C and 770°C. This indicated that the rate-limiting step changed from chemical reaction control to diffusion-control of oxygen through the boundary layer at the surface of the composites at these temperatures.

Micrographs presented by Bacos [16] show that the oxidation process at higher temperatures affected only the surface of the material. This implies that the oxidation process at high temperatures results in shrinkage of the composite due to carbon loss from the surface. In this case the oxidation triggers the formation of cracks in the matrix as well as bundle/matrix and bundle/bundle de-bonding followed by cracks within orthogonal bundles. The precise means by which the C-C composite degradation unfolds at low or high temperatures depends also on the reactivity of the matrix and the fibres. However, this can vary considerably in accordance to the manufacturing process employed to produce the C-C composite. [3]. In their investigation, Yasuda et al [17] reported that the matrix oxidation rate occurred at a higher rate than the fibres.

During aircraft operation, alkali-metal salts from marine environments and de-icing fluids can access the surface of the C-C composite materials within the aircraft braking system and act

as catalysts for the oxidation reaction and dramatically accelerate the oxidation rate [12]. Catalysts based on sodium and potassium salts have been reported to be more effective and can lead to oxidation increases in excess of an order of magnitude. This is highly alarming when considering the fact that oxidation experiments in the presence of K_2CO_3 catalyst have shown a large drop in the compression strength even after weight loss values of 2.5% and 5% [15]. The study by Duvivier et al [15] has also demonstrated that the increase in the rate of oxidation as a result of catalysis with K_2CO_3 is dependent on the catalyst content up to about 0.08%; above this figure, the rate of oxidation remains more or less constant. Therefore since only a small amount of these catalyst compounds is sufficient to cause a significant increase in the oxidation rate [4, 15], it is of paramount importance to gain as detailed as possible, an understanding of the catalytic oxidation reaction mechanism in order to devise the means to slow down, inhibit or prevent the catalytic oxidation. The enhancement of carbon gasification/oxidation has been the object of extensive studies in the last few decades owing to its use as a fossil fuel. Important insights were thus gained from these earlier studies on the catalytic effect of alkali-metals on the oxidative process. The catalytic effect of the oxides or carbonates of potassium, sodium and calcium on the oxidation of C-C composites and carbon as a fossil fuel has been reported by several investigators [4, 18, 19]. Some other important papers related to fossil fuel carbon are also reviewed here as they bear relevance to the understanding or the evolution of the understanding of the catalytic mechanism.

Adjorlolo and Rao [20] investigated the catalytic effect of K_2CO_3 and Na_2CO_3 during the gasification of metallurgical coke in CO_2 . The effectiveness of both catalysts throughout the oxidation reaction implied that some mechanism existed for the fast inward diffusion of the catalysts. In fact this observation is very similar to the behaviour of the catalysts during the oxidation of C-C composites. Since the melting point of the carbonates/oxides and of the constituent metals had not been exceeded, the authors adopted the following vapour-cycle mechanism originally proposed by Fox and White [21] to interpret the catalytic mechanism:



whereby the alkali metal (M) vapour is produced at catalyst/carbon junctions and gets reconverted to the carbonate upon contact with CO_2 . This mechanism involves formation of gaseous sodium or potassium and can mechanistically explain the movement of the catalyst

deeper into the carbon samples or the C-C composite. Thus it can explain why the catalyst can remain active throughout the entire period of oxidation. At the same time, it would be reasonable to also gradually expect some loss of the catalyst due to vapourisation of the corresponding metals. Rao et al [22] also calculated the respective thermodynamic driving force for catalysis for each carbonate by obtaining the difference in the partial pressures of sodium and potassium for the two reactions above that were proposed to be involved in the mechanism of catalysis. The higher difference for potassium led them to propose that K_2CO_3 was a more effective catalyst than Na_2CO_3 . However, according to their activation energy calculations from the experimental data of the coke gasification, the catalytic effect of Na_2CO_3 was observed to lead to a lower activation energy value than K_2CO_3 . This observation is rather unusual as in virtually all of the other investigations, K_2CO_3 has been observed to have a greater catalytic effect. As metallurgical coke by nature varies in composition and also contains several other oxides/carbonates and metals that may have a catalytic effect on gasification, it is possible that a more oxidising synergistic effect may have been active in the case of Na_2CO_3 in their investigation. In another study, Zahedi and Miller [23] discussed various potential mechanisms to explain the catalytic gasification route for carbon in the presence of K_2CO_3 . These included the redox cycle involving decomposition and reformation of the carbonate on the carbon surface and involved alkali oxides and hydroxides as intermediate compounds similar to the mechanism proposed by Adjorlolo and Rao [20]. Mims and co-workers [24-26] were the first to suggest that mechanisms that involved the formation of C-O-K complexes on carbonaceous surfaces were an essential step of catalysis as this could determine the activity of the catalyst. Other authors [27, 28] proposed the formation of a non-stoichiometric oxide with excess alkali metals that attracted oxygen from gaseous reactants and electrons from the carbon matrix to enhance the reaction of the adsorbed atoms. Further studies [29] affirmed the presence of oxygen on the carbon surface to be essential for keeping the catalyst active, thus suggesting oxygen to be involved with the catalytic process. In their investigation, Zahedi and Miller [23] also proposed surface oxygen groups to be of paramount importance to the catalytic process, thus suggesting the interactions between the catalyst and carbon to be the dominating steps during the carbon gasification process. According to Mims and co-workers [30] who studied the potassium-catalysed gasification of graphite, potassium salts reacted readily with the carbon to form surface salt complexes. K_2CO_3 was found to spread across the surface of graphite in its active mode. The same authors [30] also reported a strong interaction between the catalyst and the graphitic edges, this being comparable with cohesive bonding within the bulk of the material.

Such strong interfacial forces were thought to be responsible for the observed dispersion of the catalyst along the graphitic active edges. The oxidation of graphite was reported to proceed by recession of the layer planes. Most of these studies show evidence of some sort of interaction or bonding between the carbon and the potassium and sodium carbonate catalysts. This is also evident in the case of the catalytic oxidation of C-C composites. Fig. 2 is from the work of the present authors during catalytic oxidation of C-C blocks at 600°C and shows adhesion of K_2CO_3 particles on carbon fibres. In addition, Fig. 2 also reveals that the K_2CO_3 particles had melted or were generated from a molten phase even though the temperature of oxidation was well below the melting points of K_2CO_3 and K_2O . With this in mind, it is important to consider the research of McKee and Chatterji [31] who investigated the reactions between alkali metal carbonates and oxides with graphite in oxygen, carbon dioxide and helium atmospheres via the use of thermogravimetric (TGA) and differential thermal analysis (DTA) over a temperature range between 25°C and 1000°C. The alkali metals studied included rubidium, caesium, lithium, potassium and sodium all of which were found to catalyse the oxidation reaction of graphite. Catalytic activity commenced well below the melting point of the corresponding metal monoxide and interestingly around the melting point of their respective peroxides. Scanning electron microscopy (SEM) indicated the

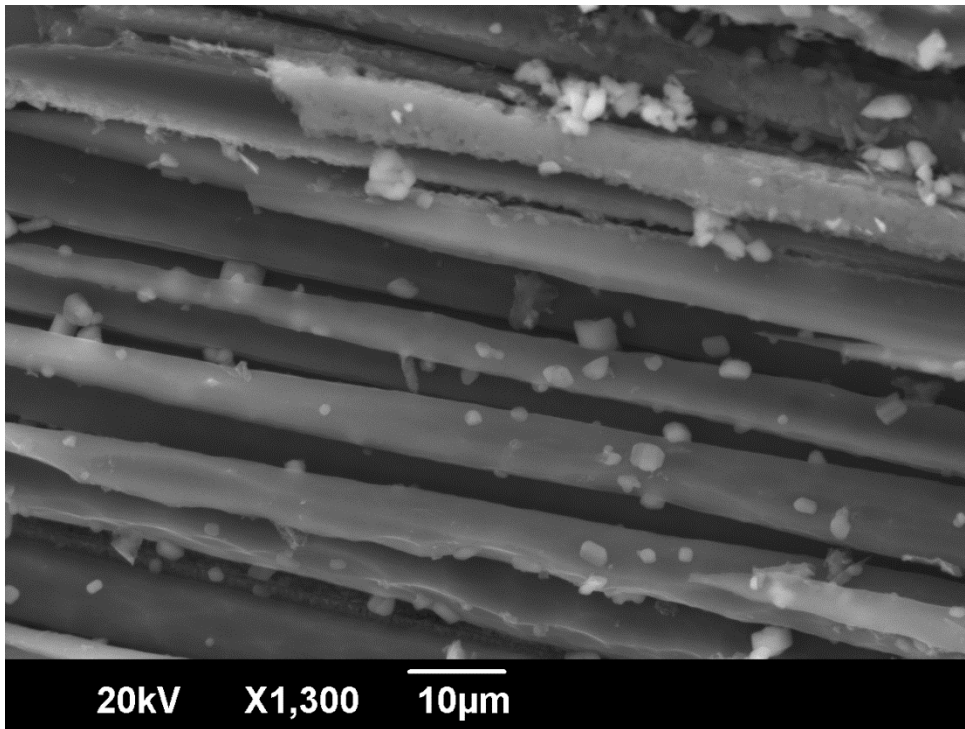
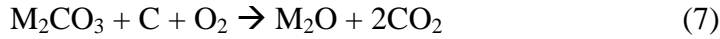


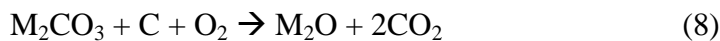
Fig. 2 Potassium carbonate particles attached to carbon fibres following oxidation of a C-C composite for 3 hours at 600°C.

presence of carbonate particles on the graphite. The carbonate particles appeared to have undergone melting even though again the oxidation temperature was below the melting temperature of the carbonate. By using thermogravimetry, McKee and Chatterji [31] also showed that the dissociation of the metal carbonate to its oxide could not take place at temperatures below 500°C. However, when the metal carbonate was mixed with graphite, the reaction



became favourable. These authors also observed the conversion of the monoxides to peroxides by means of an exothermic reaction which was followed by peroxide melting below 500°C. By using chemical thermodynamic data as compiled by Turkdogan [13], it can be shown that the dissociation of the carbonate at temperatures below 600°C is only possible in the presence of carbon. The conversion of the monoxide to the peroxide can also be shown to be possible at similar temperatures. The observed catalytic effect of the alkali metals could not be attributed to the oxide-metal-oxide type of cycle that was proposed by Fox and White [21] and by Adjorlolo and Rao [20] due to the higher chemical thermodynamic stability of the peroxides at temperatures between 400°C and 500°C in comparison to the monoxides. By combining these observations, McKee and Chatterji [31] proposed the following three-step redox cycle to account for the catalysed oxidation of graphite:

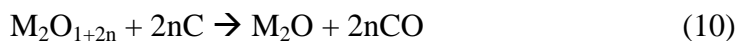
1. Carbon-induced decomposition of the metal carbonate:



2. Oxidation of the metal oxide to a peroxide:



3. Reduction of the metal peroxide to the oxide:



In the case of the alkali metals the value of n is 0.5. The catalytic effect was observed to increase going down the group in the Periodic Table due to the respective increased tendency to form the peroxide.

The catalytic effect of potassium oxide/carbonate on the oxidation of C-C composites from actual aircraft brakes was investigated by Carabiniero et al [32] who compared the weight loss between new, used and potassium oxide/carbonate-impregnated C-C samples at a

temperature range between 500°C and 900°C in air. The potassium oxide/carbonate-impregnated samples exhibited the highest weight loss at all temperatures tested indicating a strong catalytic effect. By employing in-situ electron microscopy, they observed the presence of liquid-like particles on the surface of the carbon fibres at around 650°C. In-situ X-Ray diffraction (XRD) revealed the presence of potassium oxide and/or peroxide. Their results therefore substantiated the operation of the three-step redox cycle through the formation of peroxides as postulated by McKee and Chatterji [31]. The in-situ investigation also showed that the XRD peaks of the potassium oxide/peroxide particles tended to attenuate above 700°C, indicating the formation of a thin film on the surface of the carbon as observed by in-situ microscopy. The attenuation of the peaks suggested that the peroxides were becoming amorphous. At 700°C, the formation of these particles was observed to be followed by rapid oxidation of carbon. According to Carabiniero et al [32], the oxidation of the fibres was more enhanced than that of the matrix. As for the un-impregnated samples, both new and used C-C composite samples showed negligible weight loss at 500°C. However, when subsequently tested at higher temperatures, the new C-C samples showed more prominent weight loss than the used ones. This effect became more enhanced with increasing temperature. The authors explained this finding by arguing that the most active carbon sites had already undergone gasification in the used samples. They also observed within the used C-C samples the presence of phosphorous compounds which are known to inhibit the carbon oxidation by forming an adsorbed layer that acts as a protective barrier.

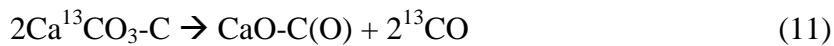
The mechanistic aspects of alkali metal-catalysed carbon oxidation were explored by Mul et al [33] who studied the molecular interactions between potassium and partially oxidised carbon black using Fourier Transform Infrared Spectroscopy (FTIR). Infrared absorption bands located around 1100 cm^{-1} were attributed to the presence of a potassium phenoxide ($\text{C}_6\text{H}_5\text{KO}$) complex; the possible presence of the compound $\text{C}_6(\text{OK})_6$ was also theorized to justify the presence of similar absorption bands. Further bands located between 1300 and 1600 cm^{-1} were attributed to a bi-carbonate species. The authors then conducted in-situ analysis of catalytic carbon black oxidation using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). They postulated that potassium salts including K_2CO_3 act as precursors for the formation of potassium oxide compounds. They attributed the absorption bands found at 1120 and 620 cm^{-1} to chemisorbed CO_2 , which formed during carbon black oxidation and strongly interacted with potassium oxide clusters. Previous studies [29, 34] had suggested that dispersed potassium oxide was bound to the carbonaceous

surface via oxygen linkages and that above 500°C the interaction of CO₂ with the species formed after decomposition of carbonates resulted in the formation of infrared absorption bands around 1110 cm⁻¹.

Strelko and co-authors [35] assumed that the catalytic gasification of carbon was the result of electron exchanges between a metal and the carbon matrix, leading to the formation of oxides of carbon and metal-carbon complexes. In particular, carbon dioxide which was liberated by the thermal decomposition of K₂CO₃ effectively activated the carbon material creating a porous structure. In other studies [36] the catalytic effect of carbonate salts was attributed to the interaction of cations with terminal proton-donor groups on the graphitic planes of carbonaceous materials. Catalytic oxidation unfolded in the presence of a porous (activated) structure, which was efficiently oxidised to form ion exchange (proton-donor) groups. Following impregnation of carbon cloth in K₂CO₃ solution, Strelko and co-authors [35] observed that the ideal temperature for activation and oxidation of the carbon material was 300°C, while at 350°C there was intensive burn-off. It was suggested that the initial carbon oxidation favoured the inclusion of potassium ions into the inter-planar space of carbon microcrystallites, enhancing their reactivity with an oxidant. The interaction between isotopically-labelled K₂¹³CO₃ and surface oxides bound on carbon was studied by Saber and co-authors [29] using Temperature Programmed Reaction (TPR). The study was performed by heating mixtures of 100 mg of various types of carbon and 10 mg of labelled K₂¹³CO₃ to temperatures up to 723°C in flowing helium. The amount of emitted CO₂ was recorded for each type of carbon. It was observed that the total CO₂ that was emitted for the K₂¹³CO₃-carbon samples was only slightly higher than the CO₂ released by the carbon-alone samples. In addition, the amount of ¹³CO₂ was similar to that for ¹²CO₂ for the K₂¹³CO₃-carbon samples; after removing the surface-bound oxygen by means of pyrolysis, production of ¹³CO₂ decreased significantly. This observation inferred that the release of ¹³CO₂ from the K₂¹³CO₃-carbon samples was not due to the decomposition of K₂CO₃ as otherwise the amount of ¹³CO₂ would have been even higher. The authors attributed the presence of ¹³CO₂ to a mechanism of isotope exchange between K₂¹³CO₃ and the surface oxides originally on carbon.

In addition to alkali-metals, alkaline-earth metals like calcium have also been reported to catalyse the oxidation of carbon. Calcium-catalysed carbon gasification was studied by Cazorla and co-authors [37] by using high-purity carbon which was loaded with CaCO₃ by

means of either ion-exchange, aqueous impregnation or through sintering. Steady-state and step-response experiments were carried out at 800°C initially in flowing helium and then in CO₂ (at a gas pressure of 0.01MPa). The authors labelled the reactant CO₂ atoms by using ¹³CO₂. They observed that the uncatalysed reaction produced equal amounts of ¹³CO and ¹²CO, as theoretically expected. However, the catalysed reaction produced unusually higher amounts of ¹²CO, but this was not the case when the reaction temperature was further increased. From this, the authors suggested that a redox cycle for the catalysed reaction involving the formation of a higher oxide is to be excluded. The CaO/CaCO₃ catalytic behaviour was in contrast to the behaviour of the alkali metals which according to McKee and Chatterji [31] and Carabiniero et al [32] form peroxides. In addition, in the work of Cazorla and co-authors [37], when the flowing gas was switched from ¹³CO₂ to helium, the desorption curves showed a continuous ¹³CO₂ and ¹³CO decay which was greater than that in the non-catalysed reaction, implying retention of these species by the catalyst-containing sample. However, CaCO₃ cannot form at the temperatures and pressure used in the experiments, implying that retention of ¹³CO₂ occurs only at the calcium-carbon interface and around CaO particles. The higher amount of ¹²CO observed during the catalysed reaction was therefore only attributable to the decomposition of CaCO₃ which was deemed the catalytically active species. The model proposed by the authors is thus summarised as:



Perhaps the most extensive investigations in recent years on the catalytic effect of potassium and calcium acetates on the oxidation of C-C composite aircraft brakes as well as graphite powder were conducted by Wu and Radovic [38]. The catalyst-loading methods for the two carbon materials were different; for the C-C composite material, catalyst loading was performed by means of impregnation in an aqueous solution of 99% calcium or potassium acetate, while for graphite powder, loading was performed by physically mixing graphite with 3 weight% of acetate. The catalytic oxidation was analysed by comparing the reaction rates of the samples at different temperatures. The reactivity, R , of the samples, defined as the rate of weight loss, $\frac{dw}{dt}$ divided by the initial weight, w_0 ,

$$R = -\frac{1}{w_0} \cdot \frac{dw}{dt} \text{ s}^{-1} \quad (13)$$

was calculated from the release rates of CO and CO₂ gaseous products. The authors observed potassium to have a much stronger ability to catalyse the oxidation reaction than calcium did. The catalytic effect of potassium was equally strong with the C-C composite material as well as with graphite powder. On the other hand, calcium acetate mixed with graphite powder showed only a limited catalytic effect. The burn-off profiles for the potassium-catalysed reaction displayed a monotonic increase in the oxidation rate for both the C-C material and graphite. On the other hand the calcium-catalysed reaction showed a monotonic decrease in the case of the C-C material and an initial decrease followed by an increase in the oxidation rate in the case of graphite. The authors also reported that the potassium catalytic effectiveness varied with different amounts of loaded catalyst, but it was insensitive to the loading method. The calcium catalytic effectiveness was attributed to an optimal initial interface contact with the carbon surface; the low wettability of the calcium catalytic species for carbon and the subsequent loss of contact during the later stages of oxidation led to a decrease in the catalytic activity of calcium. In the case of calcium there was therefore, dependency on both the amount of the catalyst loaded into the samples and the impregnation method. This feature was confirmed by further tests that showed that pre-treatment in argon enhanced the catalytic action with potassium, whereas the opposite effect was found with calcium. Both the potassium and calcium catalytically-active species were thought to undergo a redox cycle as proposed initially by McKee and Chatterji [31] and were more effective than carbon alone to adsorb and dissociate the gaseous reactants. Optimal catalysis therefore relied on the effective transportation of oxygen from the catalyst to the carbon and this was reported to be dependent upon the optimal interfacial contact between the catalyst and carbon. In order to achieve optimal catalysis, good interfacial contact between the catalytically active species and carbon must be established and maintained throughout the oxidation reaction. Potassium acetate decomposes at lower temperatures than calcium acetate and this is thought to give potassium carbonate the ability to form better contact. Moreover, potassium salts and oxide have a lower melting point than those of calcium conferring potassium salts higher mobility and thus the ability to re-disperse throughout the oxidation reaction and maintain constant optimal interfacial contact. Calcium salts and oxides have lower mobility and do not re-disperse throughout the oxidation reaction. The ability of calcium to catalyse the oxidation reaction thus relies solely on good initial interfacial contact with carbon. As the oxidation proceeds, the calcium catalytically active species progressively loses contact with carbon and thus catalyst de-activation occurs. This is the pattern observed by the authors leading to the monotonic decrease of the reaction rate of the calcium-catalysed reaction. The results of SEM

and XRD showed that the PAN fibres used in their study underwent oxidation before the matrix, in agreement with the observations of Carabiniero et al [32].

3. Mechanisms of protection of C-C composites against catalytic oxidation

Several methods have been investigated in order to develop the means to prevent or limit the catalytic oxidation of C-C composite brakes. The proposed protection mechanisms are based on three different approaches; (i) improvement of the quality of the C-C composite material, (ii) addition to the composite of compounds that can reduce the rate of oxidation and (iii) the use of coatings or physical barriers to restrict access to the C-C composite.

The improvement of the quality of the material has concentrated on the elimination of defects; this approach essentially reduces the amount of porosity and the number of active carbon sites. In addition, the conversion of amorphous carbon to the crystalline graphitic structure which is less prone to reaction with oxygen may be another possible means to enhance the oxidation resistance [39]. However, porosity is one of the features of the manufacturing method and it cannot be fully eliminated, while further heat-treatment to induce more graphitisation is likely to introduce defects in the carbon fibres and reduce their strength. Treatment of the material to improve its quality was used by Ehrburger and Lahaye [39] who observed that a lower catalytic effect could be achieved if the material was heat-treated at high temperatures up to 2623°C.

The introduction of chemical groups to the C-C composite aims to decrease the rate of carbon oxidation by reducing the rate of the mobility of the catalysts or by forming a barrier between the composite and oxygen [40]. Phosphorus compounds were thermally deposited by Wu and Radovic [40] by impregnating C-C composite samples using methyl-phosphoric acid ($\text{CH}_3\text{OP}(\text{OH})_2$) or phosphorus oxychloride (POCl_3) and heating at around 600°C. The phosphorus deposits were shown to almost completely suppress the catalytic effect of calcium, and to partially suppress that of potassium. By using XRD, SEM, X-Ray photoelectron spectroscopy (XPS) and temperature-desorption studies, the authors showed that one of the oxygen atoms from the phosphorus-based compounds was bonded onto the carbon active sites. The inhibition effect was due to a combination of site blockage whereby C-O- PO_3 and C- PO_3 groups formed a bridge-bond with the carbon through the oxygen atom and this led to the formation of a physical barrier whereby metaphosphates prevented access of the catalysts to the carbon active sites. The bridge-bond was observed to remain stable up to temperatures of 1000°C. According to Wu and Radovic [40], the catalytic activity of calcium carbonate during the initial stages of oxidation was due to the initial interfacial contact with the carbon surface; it was suggested that the presence of the C-O- PO_3 and C- PO_3

groups prevented optimal interfacial contact and therefore stopped the calcium catalytic activity. This was not the case with potassium which is much more mobile than calcium and is therefore able to re-disperse and maintain interfacial contact with the carbon for the duration of the oxidation reaction.

Boron has been reported to be another element that can be used for inhibiting the catalytic oxidation of C-C composites [42]. Wu and Radovic [41] investigated its effect by impregnating C-C samples with solutions of B_2O_3 in water followed by heating at $2500^\circ C$. The effect of this treatment was to reduce the oxide to elemental boron which had previously been reported to catalyse the conversion of amorphous carbon to graphite [42, 43]. By using XRD measurements, Wu and Radovic [41] demonstrated that the boron-doped samples had undergone more graphitisation and also exhibited three-dimensional order. According to the authors [41], substitutional boron can also enter the graphite crystal structure of the carbon fibres to make it more ordered. This has the effect of increasing the crystallite dimension which then lowers the electron density and prevents the chemisorption of oxygen. Indeed, it has been reported that the presence of boron in the carbon lattice redistributes the π electrons in the graphene plane, thus lowering the Fermi level of carbon [45]. However, the role of substitutional boron in the carbon lattice is rather controversial because studies have shown that boron itself may exhibit both an inhibiting and a catalytic effect on the oxidation of carbon [44-48]. Further investigation by the same research laboratory [48] has shown that at low levels of substitutional boron (below 2% by weight), a catalytic effect on the oxidation rate is exhibited by boron itself. On the other hand, at levels of substitution of 5% by weight, an inhibiting effect has been observed. Clearly the inhibiting effect of boron is not compatible with the observation of the redistribution of the π -electrons in the graphene layer and the lowering of the Fermi level. Therefore this warrants further investigation to understand the role of boron in the oxidation of carbon.

The observed mechanism of the inhibition by boron of the catalytic oxidation of carbon composites differs from that of phosphorus compounds. In addition, to the reduction in the Fermi level of carbon, the protective effect of boron has been proposed to occur in two ways: (i) by reduction of the number of carbon active sites and (ii) by blockage of carbon by formation of boron oxide which melts at $450^\circ C$ [41]. The effect of boron doping and of boron oxide deposition was observed by Wu and Radovic [41] to completely suppress the calcium-catalysed reaction. As with phosphorus oxide compounds, boron oxide may disrupt the initial

interfacial contact between calcium and carbon resulting in its deactivation. A combination of SEM and XRD data that were presented by Wu and Radovic [40], have demonstrated the effect of blockage of the carbon fibres and matrix by B_2O_3 . According to McKee [49], the site-blocking effect occurs because the O-O bond distance in the $-BO_3$ group is close to the distance between the zigzag carbon atoms in the graphene layer (around 0.24nm). On the other hand, results of X-ray photoelectron spectroscopy presented by Cermignani et al [50] identified the presence of boron oxycarbides rather than B_2O_3 following a four-hour oxidation at 600°C. The need for oxygen to diffuse through the encapsulating B_2O_3 or boron oxycarbides may be another factor for the reduction in the rate of the catalytic oxidation as reported by Wu and Radovic [41]. However, boron-doping and boron oxide deposition had only a minimal inhibiting effect on the potassium-catalysed reaction. It was suggested that the reason for this was the high mobility rate of potassium salts and their ability to readily re-disperse and maintain good interfacial contact with carbon. A sharp decrease in the oxidation rate after a maximum had been reached was pondered to be due to the reaction of boron oxide with potassium catalysts to form a glass-like layer, but the authors provided no data to substantiate this. However, if correct, this approach would seem to be potentially the most effective to prevent the catalytic oxidation of C-C composites. The effect of this prevention approach would be to convert the catalyst to another stable compound which would inhibit the catalysis reaction. The most likely mechanism of the catalytic oxidation of C-C composites by sodium and potassium salts is probably the one involving the redox reaction between the monoxides and the peroxides and carbon as proposed by McKee and Chatterji [31]; thus scavenging the catalyst by prevention of the reaction of alkali metal oxides to their respective peroxides would seem to be the most sensible approach to eliminate catalysis. Support for this idea is provided by the results reported by Tricot et al [51] who brushed mono-aluminium phosphate solution onto the surface of C-C samples. Following drying and a heat-treatment at 650°C in an inert atmosphere, some samples were brushed with various acetate solutions before undergoing isothermal oxidation at 650°C. After 3 hours of oxidation, the unprotected samples exhibited significant levels of oxidation; for example, the sample that had been exposed to potassium acetate lost 62% carbon, while the samples with sodium and calcium acetates lost 60% and 30% respectively. However, in the presence of these acetates, the samples that were protected with the mono-aluminium phosphate lost less than 0.5% carbon over the same period. According to the authors [51], the presence of the $Al(PO_3)_3$ coating prevented the catalysts from establishing good contact with the carbon. In addition, XRD analysis of the protected sample that had been contaminated with sodium

acetate, showed evidence of small amounts of NaAlP_2O_7 . This demonstrated the ability of the $\text{Al}(\text{PO}_3)_3$ to convert the catalytic species into an inactive compound. A similar approach was attempted by Devecerski et al [52] who added 4% by weight of boron in the glassy matrix of the composite. They showed evidence of oxidation of the boron which then formed B_2O_3 ; subsequent tests revealed inhibition against catalytic oxidation with sodium acetate. It was proposed that the inhibition to catalysis was due to reaction between B_2O_3 and Na_2O to form $\text{Na}_2\text{B}_4\text{O}_7$ thus preventing the formation of sodium peroxide. They tried to verify the formation of $\text{Na}_2\text{B}_4\text{O}_7$ by XRD and FTIR analyses, but the results were inconclusive perhaps due to the low amounts of the borate in the samples. The authors then soaked a composite sample in a saturated solution of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ for 30 minutes and subsequent oxidation runs showed results that were similar to those that had exhibited catalytic inhibition. This result provided some basis to their assumption that $\text{Na}_2\text{B}_4\text{O}_7$ could have formed and was probably the cause of the catalytic inhibition, but further work is required to confirm the mechanism.

The formation of an oxygen diffusion barrier can be generated by deposition of suitable coatings. However, in doing this care must be taken to avoid thermal mismatch between carbon and the protective coating as this may lead to the formation of cracks within the latter and this may have a detrimental effect. Oxygen can diffuse through any cracks that may form and oxidation can take place leading to the formation of further cracks and the fragmentation of the protective layer [16]. Silicon carbide and silicon nitride have thermal expansion coefficients that are close to that for carbon and therefore they represent a potential choice as protective coatings against oxidation; while they have been applied as coatings to minimise or prevent the oxidation of C-C composites, as yet there is no information on whether they can have any effect on the catalytic oxidation of the material. The use of surface treatments with phosphoric acid has been used by Labruquere et al [53] to protect C-C composites; from the data they presented, it was observed that the treated samples lost about 2% carbon after one hour at 650°C in air, in comparison to the unprotected samples that lost about 12%. It was suggested that at low temperatures the phosphorus species reacted with the catalytic impurities to form alkali and alkaline-earth orthophosphates to make the catalysts inactive. At temperatures above 600°C , the phosphorus-bearing species was reported to attach itself to active carbon sites and prevent access of oxygen to these sites. It was also reported the catalytic oxidation could not be prevented above about 900°C . At these temperatures, the

phosphorus-bearing species lost adherence with the carbon fibres and could not provide any protection.

4. CONCLUSIONS

The catalytic of oxidation of C-C composite aircraft brakes is of great concern as it can enhance the oxidation rate by an order of magnitude and thus degrade the material. The decomposition of the de-icing chemicals which are based on acetates and formates of sodium, potassium and calcium leads to formation of the respective carbonates. In the case of the alkali metals, the carbonates in the presence of carbon tend to decompose to the monoxides. Evidence in the literature has shown that the subsequent redox reaction between the monoxides and the peroxides is the mechanism of catalysis. In the case of calcium, the reversible reaction between the carbonate and the oxide appears to be responsible for the catalysis. Most of the investigations to reduce or eliminate the catalytic oxidation of C-C composites have focussed on doping the material or improving its quality, in addition to the use of protective coatings. Doping with phosphorus has been successful in stopping the catalytic activity of calcium salts by formation of C-O-PO₃ and C-PO₃ bonds. The use of boron as a dopant has shown a variety of effects; boron catalyses the conversion to graphite and also enters the lattice as a substitutional atom resulting in the reduction of the Fermi level. Both of these effects inherently increase the oxidation resistance of the material. In addition the formation of B₂O₃ around the carbon tends to block it from oxygen. Based on the current state-of-the-art, the current authors propose the use additives that will react with the alkali carbonates/monoxides and prevent the redox reaction between the monoxides and the peroxides.

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