

CORROSIVE EFFECTS OF PYROLYTIC CARBON IN GAS TURBINES

D. W. McKee and D. Chatterji

Research and Development Center, General Electric Company, Schenectady, New York 12301

In the gas turbine air is compressed to 10-20 atm., mixed with a hydrocarbon fuel, which is then burnt to form combustion gases thereby producing the thrust or shaft horsepower of the engine. A major materials problem associated with gas turbines is corrosion of alloy parts at high temperatures by salts, particularly Na_2SO_4 , resulting from reactions involving sulfur in the fuel and NaCl in the ingested air. This form of corrosion, which is most severe in the 800-1000°C range, is characterized by the formation of porous oxide scales and internal sulfides which can penetrate deep into the alloys and drastically reduce their useful life [1]. Hot salt corrosion is accelerated by the presence of particulate carbon which promotes local reducing conditions in the salt deposit and increases the sulfur activity at the alloy-salt interface. Carbon particles may arise from incomplete combustion of a liquid fuel or by catalytic decomposition of gaseous hydrocarbons and CO on the hot alloy surfaces. Even though such carbon deposits tend to burn off in the oxidizing combustion gases, the corrosive effects of pyrolytic carbon may persist for long periods [2]. In the present study the deposition, burn-off and corrosive effects of carbon on turbine superalloys have been investigated as a function of the size of the carbon particles.

The rates of deposition of pyrolytic carbon on polished metal and alloy specimens from a 10% CH_4 - N_2 stream were measured in a Mettler thermobalance, using a gas flow rate of 100 ml/min and a linear temperature rise rate of 2°C/min. After heating the specimens to 1050°C in contact with the gaseous hydrocarbon, the morphology of the resulting carbon deposit was examined by SEM. Metallic materials included Ni, Co and the Ni-base superalloys U 700, IN 713C and IN 738. The effect of alloy pre-oxidation on the kinetics of carbon deposition was not investigated. Previous studies have shown that alloys which form NiO scales are more active in promoting pyrolytic carbon formation following pre-oxidation [3].

Experiments on the behavior of carbon in Na_2SO_4 deposits were also carried out in the thermobalance by heating mixtures of powdered salt and graphite in flowing streams of air or N_2 at a linearly increasing temperature of 2°C/min. Weight changes of the mixtures were measured in both gaseous environments as functions of temperature for graphite samples in the 1 μ -2 mm size range.

Corrosion measurements were made by heating polished coupons of IN 738 ($\frac{1}{2} \times \frac{1}{4} \times 1/16$ in) in contact with Na_2SO_4 -graphite mixtures for 6 hours in flowing air at 950°C, after which time the alloy specimens were cooled and the corrosion products were examined by metallographic and electron microprobe techniques. The influence of graphite particle size on the extent and morphology of the resulting corrosion was investigated.

Even though a large excess of oxygen is normally present in the combustion gases in a gas turbine, carbon deposits are often observed to form on hot path components during engine operation. Particularly during startup fuel-oxidant mixing may be incomplete so that carbonized uncombusted fuel droplets or particulate carbon may deposit along with salt on the hot surfaces of blades and vanes. Also high stationary concentrations of gaseous hydrocarbons or CO may be present in the combustion gases even when high air/fuel ratios are employed [4]. As much as 3 percent by weight of the inlet fuel to the gas turbine may be emitted in the exhaust as unburnt hydrocarbons.

Turbine alloys, especially those containing Ni and Co, may catalyze the decomposition of such gaseous species to give pyrolytic carbon deposits which may be only slowly burnt away in the oxidizing combustion gases. Fig. 1 shows the results of TGA measurements of the rate of pyrolytic carbon formation, from a gas containing methane, on a series of metals and turbine alloys. Both Ni and Co showed high rates of carbon deposition at temperatures above 900°C, with Co exhibiting some evidence of reversible carbide formation at lower temperatures. Although deposition rates on the Ni-base superalloys were slower than on the pure metals, appreciable carbon deposition occurred at temperatures of 950°C and above for all three alloys studied. The morphology of the deposited carbon varied widely depending on the substrate material. Ni gave a granular crystalline deposit composed of columnar stacks of graphite flakes. Co gave a compact rope-like structure of tangled filaments. A fibrous mat of fine carbon threads was formed on U 700, whereas IN 738 and IN 713C developed both globular amorphous carbon masses and filamentary or whisker growth. The crystallinity, particle size and morphology of a pyrolytic carbon deposit will influence its reactivity towards oxidizing combustion gases and towards a codeposited salt phase. In particular the accelerating effect of carbon in hot salt corrosion has been shown to be strongly dependent on the particle size in the case of graphite.

Fig. 2 shows TGA data obtained in flowing air for mixtures of powdered graphite with Na_2SO_4 . A strong dependence of oxidation rate on graphite particle size is evident, with burnoff proceeding slowly over a period of hours as the temperature increased from 600 to 1000°C. With the largest particles, oxidation was still incomplete at the highest temperature. Fig. 3 shows weight changes obtained on heating graphite- Na_2SO_4 mixtures in a nitrogen atmosphere. In this case, reduction of the sulfate to sulfide, $\text{Na}_2\text{SO}_4 + 2\text{C} = \text{Na}_2\text{S} + 2\text{CO}_2$ began at temperatures close to the melting point of Na_2SO_4 (884°C) and proceeded rapidly at higher temperatures. A less marked graphite particle size effect was evident in this case, the 75 μm (325 mesh) material showing the greatest reactivity. This

pattern of behavior was mirrored by the results of corrosion experiments with the IN 738 alloys (Table I). Exposure of alloy coupons to pure Na_2SO_4 in flowing air for 6 hours at 950°C produced a thin corrosion layer consisting of an outer porous oxide scale and an inner sulfide band, the total depth of the corroded layer being about $12\ \mu\text{m}$. By contrast, addition of 25 wt. percent graphite powder to the initial salt resulted in a very marked increase in extent of corrosion even though the bulk of the graphite burnt off below 950°C . As in the TGA experiments, the $75\ \mu\text{m}$ (325 mesh) graphite showed the greatest effect with resulting sulfide penetrations of up to $140\ \mu\text{m}$.

Table I
Effects of Graphite on IN 738 Salt Corrosion
1g Na_2SO_4 + 250 mg. graphite
 950°C 6 hours in air

Graphite	Oxide/sulfide penetration μm
-(Na_2SO_4 alone)	8/12
1 μm	50/100
75 μm (325 mesh)	60/140
250 μm (100 mesh)	30/60
1-2 mm	20/40

Although these experiments were not intended to simulate conditions in an actual gas turbine, it is clear that the presence of solid carbon particles can have an important influence on the magnitude of high temperature salt-induced corrosion of turbine structural materials. The corrosive effects of carbon depend on the structure and particle size of the deposit and in general the burnoff of carbonaceous material may be slow enough for local reducing conditions to persist for extended periods in a salt condensate, leading to accelerated sulfidation of turbine alloys. Every precaution should therefore be taken to minimize carbon formation in the engine by improving combustor efficiency and by utilizing inert protective coatings on hot path components.

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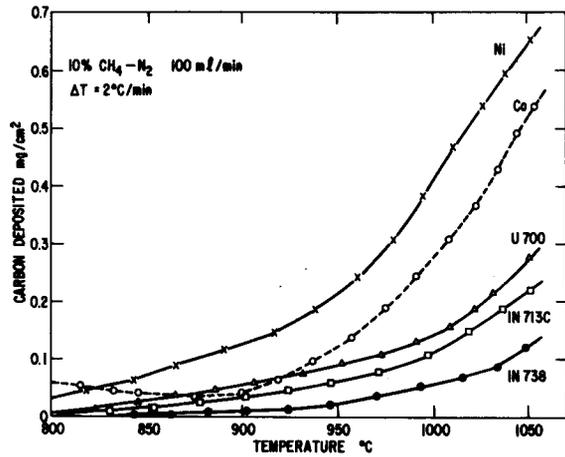


Fig. 1 Pyrolytic carbon formation on metals and alloys from $10\% \text{CH}_4\text{-N}_2$. Weight deposited vs. temperature.

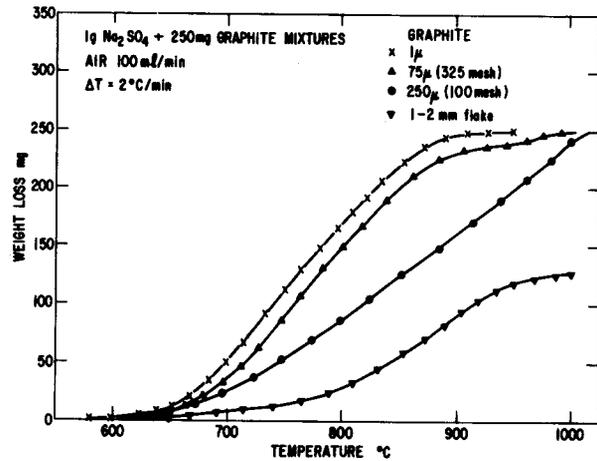


Fig. 2 Burnoff of graphite in air from Na_2SO_4 -graphite mixtures. Effect of graphite particle size.

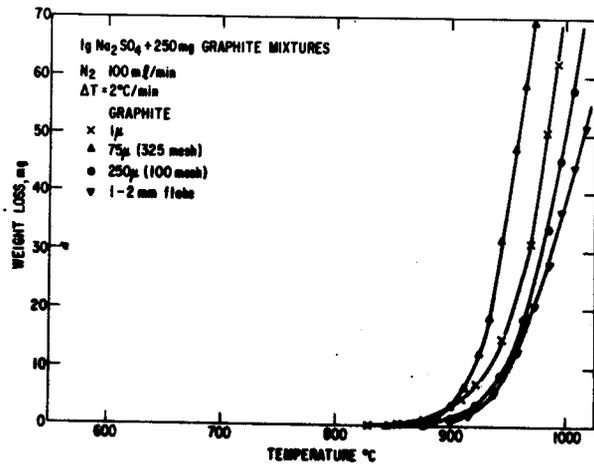


Fig. 3 Reduction of Na_2SO_4 by graphite as a function of temperature and graphite particle size.