

ACCELERATED CORROSION BY CARBON UNDER BOTH REDUCING AND OXIDISING CONDITIONS

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Carbon is unique among the common oxidants in that it is stable as a solid over a wide temperature range if the gas is sufficiently reducing. High temperature carbon corrosion is caused by carbonaceous gas species, which vary considerably with oxygen activity: hydrocarbons under reducing conditions and progressively more oxygenated species, eventually CO and/or CO₂, at higher oxygen potentials. It will be shown that the nature of the carbon corrosion reaction depends critically on the ability of the gas phase to equilibrate with respect to carbon, and on the resulting carbon activity, a_C .

At low temperatures, the exothermic reactions



produce very high carbon activities, but are kinetically hindered in the gas phase. At $T \lesssim 750^\circ\text{C}$, these gases can be supersaturated with respect to carbon ($a_C > 1$) and represent a major corrosion threat to metals which can catalyse reactions (1) or (2). Catalytically active metals include iron and nickel, so a majority of alloys can be at risk under these conditions.

Corrosion by carbon supersaturated gases results in “metal dusting”: the disintegration of sound metal into finely divided mixtures of graphite nanotubes and metal or metal carbide particles. Alloys forming protective oxide scales initially resist dusting, because the oxides are noncatalytic to reactions (1) and (2). However, eventual failure of the oxide (a process accelerated by thermal cycling [1]) allows gas access to the underlying alloy, by then depleted in the oxide scale-forming metal. Catalysis of the carbon-forming reactions leads to Fe₃C formation on ferritic alloys, and dissolved carbon in austenitics.

Nucleation of graphite is difficult, and is found to occur at energetically favoured sites, where the graphite is stabilised with its basal plane aligned with strongly oriented

planes in either Fe₃C or austenite. Nanotube growth is shown [2] to be controlled by carbon diffusion through the nanoparticles of either cementite or austenite which decorate their tips (Figure 1). The same processes occur in the bulk metal, where graphite formation disrupts the metal, producing the dust.

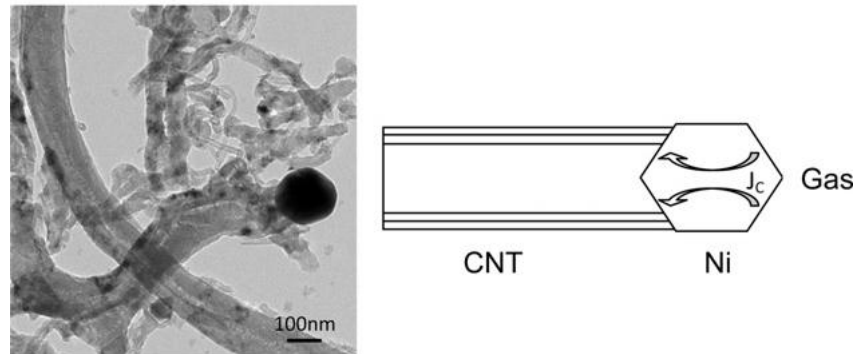
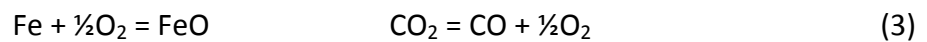


Fig.1 Nanoparticle catalyses carbon release, provides mass transfer path, and templates graphite.

In CO₂, the gas phase a_c value is extremely low, but the oxygen potential is high enough to oxidise most metals. Beneath an iron oxide scale, the equilibrium a_c value, controlled by reaction (2) and the oxygen equilibria



can be very high. In the case of Fe-9Cr exposed to near atmospheric pressure CO₂ at 650°C, $a_c \approx 0.5$ and the underlying alloy carburises [3]. At lower temperatures, the equilibrium state is approached only slowly, a_c and the volume fraction of carbide increasing with time [4]. A detailed analysis of the kinetics of reaction (2) coupled with diffusion of the resulting carbon into the alloy is shown to account for these observations.

References

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