Mechanism and Control of Carbon Deposition on High Temperature Alloys

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The commonly used anode material for solid oxide fuel cells is a cermet consisting of Ni and yttria stabilized zirconia (YSZ). Ni is an excellent catalyst for the methane activation reaction. However, Ni also catalyzes the carbon deposition reaction from carbonaceous fuels such as hydrocarbons and syngas ($CO+H_2$). Thus alternatives to the Ni-YSZ anode system are needed. The present study looks into the detailed mechanism of carbon deposition on metals and alloys. This understanding is used to develop alloys that resist the carbon deposition reaction.

Investigations of the behavior of Ni and Co in CO-H_2 environments have shown that the carbon deposition process occurs in concert with a corrosion reaction known as metal dusting. Initially, graphitic carbon deposits on the metal surface; in many regions of the surface, the graphite planes are in near-perpendicular alignment with the metal. Metal atoms are able to intercalate into the channels provided by graphite and diffuse outward to the interface with the carbonaceous environment. The fine metal particles catalyze the formation and growth of filamentous carbon (carbon nanotubes), thus continuing the metal removal and carbon formation processes. The electron micrograph in figure 1 is an example of an interface where the carbon deposition/metal dusting reaction is in progress. An additional carbon deposition reaction that is operative involves the diffusion of carbon into the metal interior followed by the precipitation of graphite within the metal whereby the metal mechanically breaks up.

The development of high temperature alloys that could resist the carbon deposition/metal dusting reaction is largely based on alloy compositions that form an in-situ surface film of chromium oxide at high temperatures in the carbonaceous environment. However, in highly reducing carbon-rich environments such as syngas, a protective chromium oxide layer is, in most cases, not able to establish itself rapidly enough to prevent carbon intrusion. Since the growth of oxide layers on alloy surfaces is controlled by the mixed ion-electron conduction characteristics of the oxide, this aspect has been used to develop alloys that resist carbon deposition. In the alloy, 20Fe-40Ni-10Mn-30Cr, a layer of MnO forms almost instantaneously when exposed to a $50CO$-$50H_2$ environment at 850°C. In the above environment, MnO is an n-type conductor and allows rapid Mn transport via Mn vacancies. Beneath this MnO layer, a diffusion resistant, adherent $MnCr_2O_4$ film develops and provides long-term resistance to carbon transfer as shown in figure 2.

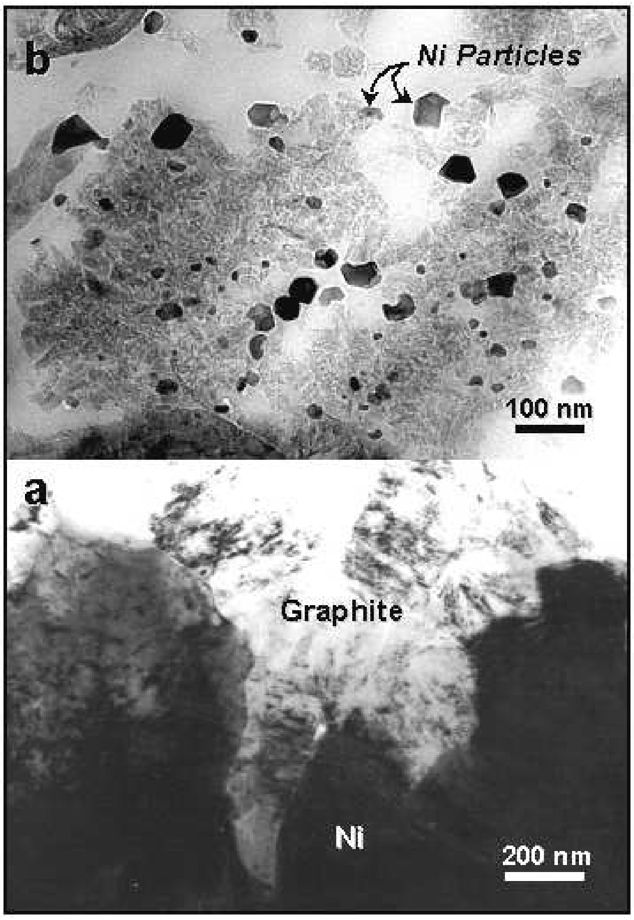

Figure 1. Cross sectional TEM images showing (a) the interface between nickel and graphitic deposit and (b) filamentous carbon at the outer region of carbon deposit.

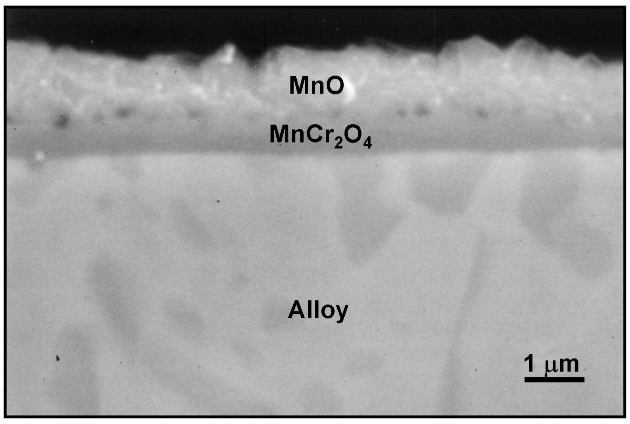

Figure 2. Cross sectional SEM image showing two-layered surface oxide resistant to carbon deposition.