ABSTRACT

In high temperature solid oxide fuel cells when natural gas is used as a fuel, high carbon activity environments can be encountered in the anode compartment. Under these conditions, nickel could corrode by a process, known as metal dusting. In the present study, metal dusting corrosion of pure nickel is simulated in high carbon activity environments at temperatures between 350°C and 1050°C. The focus of this research is to understand reaction mechanisms by characterizing interfacial processes at the nano level. Nickel corrodes by a combination of carbon intrusion and precipitation in the bulk metal and atom migration through surface carbon deposits. The nature of the carbon deposit is important in the overall corrosion process. At lower temperatures close to about 350°C, nickel forms a carbide, \( \text{Ni}_2\text{C} \), which is easily destabilized and makes an additional contribution to the corrosion mechanism.

INTRODUCTION

In solid oxide fuel cells, the preferred anode electrode is a cermet of Ni-ZrO\(_2\) (1). In systems where natural gas is used as a fuel, high carbon activity environments can be encountered in the anode compartment. In strongly carburizing atmospheres at high temperatures, nickel can corrode by a process, known as metal dusting, which is the carbon-assisted disintegration of bulk metal into metal powder. Such corrosion has been observed in processes in chemical and petrochemical industry where hydrocarbons or other strongly carburizing atmospheres are encountered. Early work on metal dusting of steels as well as Fe and Ni base high temperature alloys was done by Hochman (2). More recently, Grabke and co-workers have significantly extended the understanding of the phenomena underlying metal dusting corrosion (3).

The Hochman proposal for the metal dusting corrosion of iron which has been further elaborated and refined by Grabke and co-workers, involves the initial formation of a metastable \( \text{Fe}_2\text{C} \) carbide layer in the carbon supersaturated environment. The carbide subsequently dissociates when it is destabilized by carbon deposition, leading to the formation of “dust”. Ni and Ni base alloys are also subject to metal dusting; however, their disintegration leads to larger metal particles, the overall rate of metal wastage is lower and the carbon deposition is less. Previous work (4) indicates that the mechanism of metal dusting of Ni is different from that for iron and steel because the metastable surface carbide layer that typifies Fe corrosion is not observed in the case of Ni.
However, Ni still corrodes by a combination of atom migration through surface carbon deposits and carbon intrusion and precipitation in the bulk metal.

A well-known reaction between carbon and transition metals is the metal mediated transformation of amorphous carbon into graphite, which has generally been called catalytic graphitization (5). Recently, it has been reported that catalytic graphitization of amorphous carbon in contact with a solid metal such as Ni or Co can take place below 900°C (6,7). The most widely accepted mechanism to explain these phenomena is a solution precipitation mechanism (8), where carbon dissolves and supersaturates the metal and then precipitates as graphite. The overall reaction is driven by the free energy difference between the amorphous and crystalline states of carbon.

Our study is in agreement with this mechanism in an overall sense. However, probing the corrosion interface at the nano level raises several interesting questions. In this paper, based on the microstructure of metal dusted Ni samples at various temperatures, a mechanistic picture is presented which also attempts to explain the influence of reaction layers and forms of carbon on the corrosion process. Additionally, some understanding is developed on the role of surface orientation of metal in the overall corrosion.

**EXPERIMENTAL APPROACH**

In the present study, both polycrystalline Ni (Alfa Co., 99.99% purity) and single crystals (Monocrystals Co., 99.99% purity) were selected for investigation. Both Ni foils with a thickness of 100 µm and bulk Ni were used typical of the as-received condition. Single crystals had two surface orientations, (100) and (111). The specimens were discs of 9.6x0.5 mm; the faces were polished by Linde B and cleaned ultrasonically in acetone.

The sample to be corroded was hung from a Cahn 1000 electrobalance by means of a platinum suspension wire. The balance was attached to a vertically placed quartz reactor tube; the kinetics of corrosion was measured by thermogravimetric analysis (TGA). A platinum resistance furnace surrounded the quartz tube; the furnace could be moved up to bring the sample to reaction temperature and moved down to cool the sample. The reaction gas mixture entered the reactor at the bottom and escaped at the top where it mixed with an argon stream used to provide an inert environment within the electrobalance assembly. At the start of an experimental run, the sample was hung from the electrobalance and the quartz reactor tube slid into place with the furnace in the “down” position. The reactor tube was kept under a purging argon stream, and the furnace brought to the reaction temperature, the sample still being held at room temperature. The argon flow was then replaced by hydrogen gas and the furnace was hydraulically lifted up around the sample so as to position it within the constant temperature zone (±1°C) of the furnace. It took approximately 15 min for the sample to attain the experimental temperature. Hydrogen was used to reduce any surface oxide that could be present on the sample surface. Once a constant mass was recorded by the electrobalance (~ 10 min) the hydrogen was replaced by the corrosion gas mixture, the flow rate being high enough (~ 100 cc/min) so that mass transport in the gas phase would not be rate controlling.
CO/H₂ gas mixtures of two ratios, 25 and 1, were used as the carbon supersaturated gas environment. The corrosion measurements were carried out in the 350°C - 1050°C temperature range, for times extending up to ~100 hours. After corrosion, some of the samples were mounted vertically in an EpoFix embedding media. The cross-sectional morphology of the corrosion interface was examined by JEOL 840A scanning electron microscope (SEM). Cross sectional transmission electron microscopy combined with microdiffraction and microchemical analysis was used to investigate the reaction interfaces at the nano level. A sandwich structure with the specimen in the middle was created using epoxy glue and glass. Discs of 100 μm thickness were then cut and polished from the sandwich. These were dimpled and ion-milled to generate electron transparent areas. Micrographs were taken using a Philips CM200/FEG transmission electron microscope (TEM).

RESULTS AND DISCUSSION

In all the Ni specimens investigated qualitatively similar phenomena are observed, but the details vary depending on temperature and gas phase chemistry.

In CO/H₂ Mixture at a Ratio of 25

Fig. 1a shows the typical microstructure of polycrystalline bulk Ni having an average grain size of 50 μm. Fig. 1b shows a cross sectional view after 46 hours of metal dusting corrosion at 750°C and a CO/H₂ ratio of 25. The interface region reveals carbon deposit on the Ni substrate. Most surfaces of the polycrystalline Ni grains appear to be serrated by intrusion of carbon. The precipitation of graphite is observed inside the bulk Ni. The progress of graphite growth is inhomogeneous and regions of metal become encased in graphite forming relatively large metal particles (>0.5 μm) in the carbon deposit. These particles are probably dislocated from the metal during graphite growth. This process is possible if continuous transfer of carbon from the gas atmosphere occurs to form metal-carbon solid solution. Metal particles dislocated from bulk metal in this manner undergo further disintegration with continued carbon transfer.

Since metal dusting is accompanied by carbon deposition, TGA data (Fig. 2) provide some measure of the corrosion intensity based on the mass gain due to carbon dissolution and deposition. In Fig. 2 shows the mass gain for polycrystalline Ni samples reacted at a CO/H₂ ratio of 25 and 750°C, 650°C and 375°C, respectively. However, the actual quantification of metal loss is difficult by TGA. In order to measure the metal dusting rate more accurately the Ni sample used in the corrosion studies is first sputter-deposited with a very thin strip of inert metal. The coated area is non-catalytic to carbon deposition and therefore does not undergo metal dusting. The metal recession with respect to the inert metal coating is measured in SEM images and the corrosion rate is calculated with high accuracy. Both general and localized rates can be obtained by this technique. For example, the Ni sample in Fig.1 has a metal recession of about 14 μm therefore, the general metal dusting rate is 75 mil per year.

Bright field TEM image reveals, in addition to metal particles, a mixture of graphitic carbon, amorphous carbon and filamentous carbon in the corrosion product. The detail of the metal dusting attack on a Ni grain is shown in Fig. 3. A cross sectional TEM bright
field image and a corresponding selected area electron diffraction (SAED) pattern at a beam orientation of B= [111] are presented. The Ni foil was metal dusted at 550°C for 7 hours at CO/H₂=25. The carbon layer next to Ni is predominantly graphitic (~80 pc.), the rest being amorphous. The development of a serrated metal surface, i.e. the irregular disintegration, is mainly caused by intrusions of graphite which penetrate into the metal phase. The structure of graphite region observable under diffraction contrast conditions indicates an oriented growth of the atomic planes of graphite perpendicular to the original metal surface. This observation corresponds to the features occurring in the zone of cementite decomposition reported in previous studies of metal dusting of iron (9), thus suggesting a similar disintegration mechanism. However, in the case of Ni, there is no carbide phase detectable at the reaction front, indicating that Ni corrodes without the formation of a compound phase. In the area of graphite layer, energy dispersive X-ray spectroscopy (EDXS) reveals Ni with mass content of about 1.8%, thus indicating a partial dissolution of the metal similar to the observations in iron. Therefore, Ni atoms intercalate into graphite, diffuse outward to the interface with gas phase where they coalesce to minute Ni particles, which catalyze and are carried away by filamentous coke.

Details of the filamentous coke region of the same specimen are shown in Fig. 4, which reveals relatively small Ni particles (5-80 nm) in the outer reaction zone. These can form by agglomeration processes of atomic Ni from the graphite layer. The coke may have different shapes, growing as cones, tentacles, and leeches and is composed often of fine carbon filaments growing behind the catalytic particle which is situated at its top. The morphology of coke is mainly controlled by hydrogen, where hydrogen allows open forms of carbon such as filaments to be produced. Without hydrogen, carbon will deposit in closed forms such as shells (10).

**In CO/H₂ Mixture at a Ratio of 1**

Fig. 5a shows the cross section of the graphite deposit and penetration in Ni foil formed after 7 hours of metal dusting corrosion at 950°C and a CO/H₂ ratio of 1. Most surfaces of the polycrystalline nickel grains appear to be smooth with graphite deposition; basal graphite lattice planes are oriented parallel to the surface. This parallel orientation of graphite was also confirmed by cross sectional TEM. Reactions between hydrocarbons and transition metals at around 1000°C result in the formation of crystalline graphite also known as highly oriented pyrolytic carbon (11). Current work also shows that temperatures above 800°C yield well-crystallized, ordered graphite. However, some grains are serrated by intrusion of carbon, where large Ni particles catalyze filamentous carbon formation. A massive precipitation of graphite is observed inside the Ni foil. A bright field TEM image of the same sample is shown in Fig. 5b. The graphite precipitates inside the Ni grain and a large Ni particle is detached from the grain where the basal planes of graphite are aligned in perpendicular to the Ni surface as indicated by an arrow. Therefore, Ni disintegrates into metal powder during the corrosion reaction by catalytic graphitization. In this mechanism, carbon dissolves and diffuses into nickel, supersaturates it, leading finally to profuse graphite precipitation within the bulk Ni. Significant bulging of the sample of the metal often accompanies such precipitation. In many regions, such graphite precipitation leads to undercutting and detachment of metal.

Fig. 6 shows the bulging of Ni foil, where the thickness change of Ni foils was measured after 7 hours of reaction from 450°C to 950°C at a CO/H₂ ratio of 1. A cross
sectional SEM image of Ni foil after metal dusting corrosion at 550°C for 7 hours at CO/H2=1 is shown in Fig. 7 along with the image of the as-received Ni foil before reaction. Such bulging has been observed in Ni foils reacted at a CO/H2 ratio of ~1 and not at a CO/H2 ratio of ~25. This suggests that the principal carbon transfer reaction is: CO + H2 = C + H2O. The forward rate of this reaction is expected to be proportional to the product of CO and H2 partial pressures and attains a maximum when their concentrations are equal, corresponding to a ratio of 1.

The Effect of Surface Texture on Graphite Deposit

The inward growth and deposition of graphite are strongly dependent on the surface orientation of the crystal grains. The fundamental starting mechanism on the atomic scale appears to be graphite texturing, with basal graphite lattice planes perpendicularly oriented to the Ni surface acting as channels for the disintegration process. In order to investigate the effect of surface orientation of metal on the nature of graphite deposit, two different surfaces of Ni single crystals were exposed to CO/H2 mixture at a ratio of 25 for 1 hour at 650°C. As shown in Fig. 8, cross sectional TEM image of Ni (111) plane and carbon interface reveals that basal planes of graphite are aligned parallel to the Ni surface. High resolution TEM image on Ni (111) surface shows the lattice fringes of graphite basal planes. The hexagonal lattice constant of the Ni (111) plane is 2.49 Å and the hexagonal lattice constant of the graphite basal plane is 2.46 Å. Therefore, the carbon is arranged in graphite layers with the epitaxial relationship of (0001) Graphite // (111) Ni; [1120] Graphite // [110] Ni (12). In contrast, Fig. 9 shows the image of Ni (100) plane and carbon interface, indicating that hexagonal graphite planes tend to be aligned perpendicular to the Ni surface. Therefore, the interspace between graphite planes provides channels for the migration of Ni atoms. At the interface with the gaseous environment, the Ni atoms coalesce to small particles, which catalyze filamentous carbon that transports the metal particles away. The penetration of the graphite planes into Ni (100) surface suggests that especially the free ends of these lattice planes favor the disintegration of Ni. The Ni (111) surface tends to favor the precipitation of graphite planes in parallel alignment to the surface, thus blocking the metal migration path. However, texture or preferred orientation has an effect only on the initial corrosion process for no longer than 7 hours. The texture effect is not retained in the long term to be of any practical significance.

Fig. 10 shows the cross sectional TEM image of Ni (111) plane and graphite interface after metal dusting corrosion of Ni foil at 550°C for 7 hours at CO/H2=1. It reveals that hexagonal graphite planes are aligned parallel to the Ni surface as in the case of Ni (111) single crystal, but the faceted edge of graphite are observed. Therefore, the disappearance of texture effect can be rationalized with this observation. Due to the initial defects on a crystalline surface such as kinks and steps, the buckled edge of graphite can be formed. At these edges where the formation of epitaxial graphite layer is not preferred, carbon atoms dissolved in bulk Ni attach to graphite basal planes. Thus, the bulk metal is attacked by the inward growing graphite. This process is schematically illustrated with three steps: (i) deposition of graphite on the Ni surface in different orientations from supersaturated solid solution of carbon and Ni, (ii) growth of graphite into the Ni by addition of carbon atoms from the solid solution to the surface steps where graphite basal planes are perpendicular to the surface, (iii) destroy of the Ni by the inward growing graphite under transfer of metal particles into the coke layer. The epitaxial relationship
between the different Ni orientations and the graphite deposit has also been investigated by other researchers. A theoretical study from extended Hückel molecular orbital calculations showed that the Ni (111) and Ni (311) surfaces provide better epitaxial conditions for graphite formation than the Ni (110) and (100) orientations (13). However, TEM investigation of CVD graphite on Ni showed that the graphite deposits were oriented with their basal planes parallel to the Ni surface irrespective of the Ni orientation used (14).

**Ni$_3$C Formation at Lower Temperatures**

At lower temperatures close to about 350°C, nickel forms a nickel carbide, Ni$_3$C. Fig. 11 shows Ni$_3$C layer on Ni surface after reaction at 375°C for 65 hours in having a CO/H$_2$ ratio of 25. The present observation agrees quite well with previous results where Ni$_3$C was observed on Ni films carburized in CO gas at 300°C. The carbide decomposed completely at 430°C (15). Selected area electron diffraction patterns have been taken in the current study at beam orientations of B=[101] Ni and B=[100] Ni$_3$C, respectively. A high resolution TEM image of the Ni/Ni$_3$C interface shows high angle tilt boundaries and misfit orientation. The angle of misfit between 2.03Å lattice fringes of Ni and 2.28Å lattice fringes of Ni$_3$C is small (~8.5°). Ni$_3$C layer is easily destabilized and makes an additional contribution to graphite formation. The corrosion mechanism under these conditions can be very similar to that of Fe. Once amorphous carbon deposits, Ni$_3$C dissociates into Ni atoms and carbon. Graphite nucleation occurs at this corrosion front and the graphite grows into the amorphous carbon, consuming it.

**SUMMARY**

Bulk nickel disintegrates into metal particles in high carbon environments by a corrosion reaction at temperatures above ~350°C. The metal dusting corrosion mechanism of Ni is different from that of Fe. Above 350°C, no nickel carbide exists. However, nickel gets supersaturated with carbon since the solubility is rather low. This is followed by graphite deposition on the surface in different orientations and graphite precipitation within the bulk Ni leading to bulging. In many regions, such graphite precipitation leads to undercutting and direct detachment of metal particles. Direct graphite growth into the metal phase is controlled by the attachment of carbon atoms from the supersaturated solid solution to graphite basal planes. Further disintegration of the nickel particles has been observed where nickel atoms intercalate into graphite and diffuse outward to the interface with gas phase. At this interface Ni atoms coalesce to minute nickel particles, which catalyze and are carried away by filamentous coke. At lower temperatures close to about 350°C, nickel forms a carbide, Ni$_3$C, which is easily destabilized and makes an additional contribution to graphite formation.
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**Fig. 1.** Cross sectional SEM images of (a) as-received polycrystalline bulk Ni and (b) interface between Ni and carbon showing graphite, filamentous carbon, and Ni dust particles after reaction at 750°C for 46 hours at CO/H2 = 25.
Fig. 2. TGA data for polycrystalline Ni samples at 750°C (●), 650°C (■) and 375°C (○) at CO/H₂=25.

Fig. 3. Cross sectional TEM image showing the interface between carbon (graphite and amorphous carbon) and Ni grain with SAED pattern at B=[111] after reaction at 550°C for 7 hours at CO/H₂=25.

Fig. 4. Cross sectional TEM image showing the interface between filamentous coke and carbon after reaction at 550°C for 7 hours at CO/H₂=25.
Fig. 5. Cross sectional images of a Ni foil by (a) SEM and (b) TEM showing graphite deposit and penetration after reaction at 950°C for 7 hours at CO/H₂=1.

Fig. 6. The thickness change of Ni foils as a function of temperature after reaction for 7 hours at CO/H₂=1.

Fig. 7. Cross sectional SEM images of Ni foils showing (a) as-received foil and (b) bulging after reaction at 550°C for 7 hours at CO/H₂=1.
Fig. 8. Cross sectional TEM images and schematic at the Ni/carbon interface showing that basal planes of graphite are aligned parallel to the Ni (111) surface after reaction at 650°C for 1 hour at CO/H₂=25.

Fig. 9. Cross sectional TEM image and schematic at the Ni/carbon interface showing that basal planes of graphite are aligned perpendicular to the Ni (100) surface after reaction at 650°C for 1 hour at CO/H₂=25.
Fig. 10. Cross sectional TEM image at the Ni (111) surface showing multiple steps after reaction at 550°C for 7 hours at CO/H₂=1 and schematic representations of the progress of metal dusting corrosion.

Fig. 11. (a) Cross sectional TEM image showing Ni₃C layer on Ni surface after reaction at 375°C for 65 hours at CO/H₂=25. (b) HREM image of the Ni/Ni₃C interface showing misfit orientation in lattice fringes. Selected area electron diffraction patterns at beam orientations of (c) B=[100], Ni₃C and (d) B=[101], Ni, respectively.