CORROSION STUDIES OF IRON, NICKEL AND INCOLOY 800 IN SODIUM-POTASSIUM NITRATE MELTS AT 250-550°C

Hector Fernandez, J. Malcolm Carter and R. A. Osteryoung
Departments of Chemistry and Division of Restorative Dentistry, State University of New York at Buffalo, Buffalo, New York 14214

ABSTRACT

The corrosion behavior of iron, nickel and Incoloy 800 alloy (1800) electrodes in molten (Na,K)NO₃ has been investigated over a temperature range of 250-550°C. Anodic polarization curves as well as open circuit potential measurements for Fe, Ni and 1800 show evidence of spontaneous passivation when these metals are in contact with the melt at any temperature studied. Intergranular corrosion and pitting have been found in 1800 at potentials more anodic than the steady state potential, this phenomenon being more important at the lowest temperature investigated (250°C), than at the highest (550°C). Results of metallographic examination of the samples are presented.

INTRODUCTION

Studies of the corrosion behavior of possible container materials are quite important as part of the development of molten (Na,K)NO₃'s as heat transfer fluids in solar collectors at temperatures in the range 250-550°C (1). Although corrosion of iron, nickel, some steels and to a lesser extent chromium has been studied in molten nitrates, most of these studies involve temperatures well under 550°C and results are not directly applicable to high temperature, molten salt receiver systems (2-7). Literature data indicates that iron and nickel passivate spontaneously in contact with the (Na,K)NO₃ melt giving no detectable amount of ionic species of the metals in the fused salt. Passivating films are mainly magnetite (Fe₃O₄) and NiO. Although the long term corrosion behavior of Incoloy 800 (1800) in molten nitrates in closed loops has been studied (8-10), no electrochemical studies appear to have been carried out on this material. 1800 appears to be a suitable container over the temperature range proposed for operation of solar receivers using the molten nitrates as heat transfer fluids.

RESULTS AND DISCUSSION

Open circuit potentials and polarization curves for Fe, Ni and 1800 were measured at various temperatures. A gold pseudo-reference electrode was employed in these studies. In the case of iron, nitrite
oxidation can be seen and an apparent limiting current is achieved. As iron is polarized further anodically, an initial passive region is formed (Figure 1). The E-log i curves appear to show Tafel behavior for about one decade. Massive evolution of a brown gas, presumably NO₂, starts to appear in this range. Beyond the Tafel region, the electrode depolarizes sharply, indicating a breakdown of passivity. For experiments at 548°C, the E-log i curves are complex and not terribly reproducible. Initial cathodization of the electrode eliminates the initial passive region.

The behavior of nickel is complex; breakdown of the passive film is rather sharp depending on the anodic potential to which the polarization is carried. For instance, polarization of Ni to +0.73 V vs the Au reference gives a retrace, on scan reversal, of the initial anodic polarization curve. The surface is covered by a thin blue/black film. Scan reversal on anodic polarization at +0.78 V, however, yields continuing increasing currents (Figure 2). The electrode develops pits which spread on its surface, and a thin black film.

With I800, polarization curves somewhat similar to those for Fe are obtained; the limiting current for the oxidation of nitrite is not as well defined at the I800. However, the most striking observation is the fact that a sharp breakdown potential is observed at lower potentials than for iron, and that these breakdown potential decrease - are less anodic - at lower temperatures. Such a polarization curve is shown in Figure 3 for 250°C. If the potential scan is reversed after the breakdown potential, one obtains a closed current loop, the size depending on the reversal potential. After such experiments the melt shows an orange color, and dichromate ion was determined to be in the melt. As the temperature is increased, the closed current loop, even after entering an apparently unpassivated region, is much smaller than those obtained at lower temperatures, indicating the initially passive film is quickly reformed. Figure 4 shows such a polarization curve at 547°C.

Metallographic examination of the I800 shows marked dependence on the temperature and polarization conditions. At 250°C, no significant change in the surface can be observed at the open circuit potential. Polarization to potentials where nitrite is oxidized forms a transparent, light-blue film on the surface. At potentials slightly more anodic than the breakdown potential, the electrode surface shows very defined grain boundaries as well as pits spread out over the surface. Figures 5 and 6 show unetched and etched views of the same field of an I800 sample taken into the breakdown region and cycled at 250°C. Fissures seen in Figure 5 are shown to be intergranular cracks in Figure 6 caused by dissolution of chromium depleted regions in grain boundaries. An SEM photograph in Figure 7 shows evidence of pitting and intragranular cracking as well. This would not be as deleterious to mechanical properties as the intergranular attack. The more anodic the potential, once the breakdown potential is attained, the stronger
the surface attack. Above 350°C, a thin transparent brown/blue film is observed, which becomes more intense as the temperature increases. The higher the temperature, the thicker the film formed. At potentials more anodic than the nitrite oxidation wave, pits as well as a brown/black film are observed. At 547°C, the highest temperature studied, no pits were found under any conditions; a very thick brown film is obtained after anodic polarization experiments to +1.54V vs the Au reference. Figure 8 shows an electrode polarized at 547°C. A thick brown oxide film is formed, but no pitting is evident. Table I shows open circuit potentials and breakdown potentials, obtained as that potential where the anodic current undergoes a sharp increase.

Table I

Open circuit potentials, vs Au reference, and breakdown potentials for Fe, Ni and I800 at various temperatures.

| T, °C | E_{OC} (V) | E_{B} (V) |
|------|------------|-----------|
|      | Iron       |           |
| 258  | -0.277     | +1.23     |
| 345  | -0.200     | +1.31     |
| 398  | -0.040     | +1.49     |
| 548  | -0.015     | - (not observed) |
|      | Nickel     |           |
| 345  | -0.105     | -         |
| 398  | -0.030     | +0.78     |
| 548  | +0.002     | -         |
|      | I800       |           |
| 250  | -0.300     | +0.85     |
| 350  | -0.100     | +0.98     |
| 452  | -0.030     | -         |
| 500  | -0.017     | - (not observed) |
| 547  | -0.005     | -         |

I800 samples etched in oxalic acid at high current densities showed similar etch-pit formation to those found in the molten nitrate at 250°C. Grain boundaries were observed to have been heavily attacked and within the grains etch pits (geometric-sided depressions) were formed in areas of high dislocation densities and erosion has occurred around the TiC/N phases of the I800. These observed microstructures, though not showing as severe surface deterioration as those produced in the molten nitrate bath at 250°C, have similar features. A protective passivating oxide film has been unable to develop or be maintained, and the chromium depleted grain boundary regions which would have
provided a pathway for slow chromium diffusion to the surface under film forming conditions have dissolved. As Bradshaw has indicated (10), 1800 under static, long term conditions in the molten nitrate at 530°C had an outer iron oxide layer, probably Fe₃O₄, and a continuous layer beneath it which appeared to be a mixed spinel oxide, Fe(Fe, Cr)₂O₄. Sub-surface discontinuous phases consisted of a Cr-rich oxide phase, and apparently a pure Ni phase. It thus appears that 1800 is protected by a much more protective oxide film at higher temperature than at lower, at least over the 250-550°C range. Very recent work by Bradshaw on corrosion of 1800 in a thermal convection loop molten nitrate has indicated the formation of pits on a coupon immersed for approximately 5000 hours at 333°C (11). He reports that the pits appear to have sharply defined boundaries, indicating attack on individual grains. Thus, the electrochemical experiments appear to be in general accord with these most recent long-term corrosion studies.

ACKNOWLEDGEMENT

We would like to acknowledge helpful discussion with Dr. Robert Carling and Dr. Donald Nissen of Sandia National Laboratories.

CREDIT

This work was supported by Sandia National Laboratory.

REFERENCES

1. L. N. Tallerico, SAND 79-8015, Technical Report, Sandia Laboratories, Livermore, California, August, 1979.
2. A. J. Arvia, J. J. Podesta and R. C. Piatti, Electrochim. Acta, 17, 33 (1972).
3. T. Notoya and R. Midorakawa, Denki Kagaka, 41, 865 (1973).
4. A. Conte and S. Casadio, Rec. Sci., 36, 343 (1966).
5. H. S. Swofford and H. A. Laitinen, J. Electrochem. Soc., 110, 814 (1963).
6. A. A. El Hosary, A. Baraka and A. I. Abdul-Rahman, Brit. Corres. J., 11, 228 (1971).
7. B. J. Brough and D. H. Kerridge, Inorg. Chem., 4, 1353 (1965).
8. R. W. Bradshaw, Abstract No. 210, The Electrochemical Society, Fall Meeting, Denver, Colorado, October, 1981.
9. R. W. Carling, L. M. Kramer, R. W. Bradshaw, D. A. Nissen, S. H. Goods, R. W. War, J. W. Munford, M. M. Karmowsky, R. N. Biefeld and N. J. Norem, SAND 80-8052, Sandia National Laboratories, Livermore, California, March, 1981.
10. R. W. Bradshaw, SAND-8210, Sandia National Laboratories, February, 1982.
11. R. W. Bradshaw, SAND82-8911, Sandia National Laboratories, January, 1983.
Fig. 1. E-log $i$ curves for IRON.
T = 250°C, ---, $+1.17$V (precathodized at $-0.80$V); (☐) T = 398°C, --- $+1.48$V.

Fig. 2. E-log $i$ curves for NICKEL;
--- $+0.73$V. --- $+0.78$V. T = 345°C.

Fig. 3. E-log $i$ curves for 1800;
---$+0.85$V, ---$+0.88$V, ---$+0.95$V.
T = 250°C.

Fig. 4. E-log $i$ curve for 1800;
---$+0.46$V, ---$+0.84$V, ---$+1.20$V.
T = 547°C.

472
Fig. 5. Electrode, sectioned cross section, 250°C, 4 hr. Unetched.

Fig. 6. Same as Fig. 5; same field of view. Etched.

Fig. 7. Same as Fig. 5; SEM.

Fig. 8. Electrode, sectioned cross section of 547°C. Etched.