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X-Ray Diffraction Analysis of Corrosion Products of FE-NI-CR Alloys Formed In Molten Nitrate Salts

D. R. Boehme and R. W. Bradshaw

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X-RAY DIFFRACTION ANALYSIS OF CORROSION PRODUCTS
OF FE-NI-CR ALLOYS FORMED IN MOLTEN NITRATE SALTS

D. R. Boehme and R. W. Bradshaw
Sandia National Laboratories, Livermore
Exploratory Chemistry Division I

ABSTRACT

Chemical phase identifications of complex, multilayered corrosion products formed on Fe-Ni-Cr alloys immersed in molten NaNO_3 - KNO_3 and LiNO_3 - NaNO_3 - KNO_3 were obtained by X-ray diffraction analysis. Diffraction analyses performed after successive material removal steps provided depth profiles of corrosion products and identified the dominant phases as NaFeO_2 , Fe_3O_4 and Cr_2O_3 for Alloy 800 and 316SS after immersion in NaNO_3 - KNO_3 . In LiNO_3 - NaNO_3 - KNO_3 , the major corrosion products identified on Alloy 800 were LiFeO_2 , Fe_3O_4 and Cr_2O_3 . X-ray diffraction results were supplemented by electron microprobe analyses which revealed the solid solution nature of several of the oxide phases.

CONTENTS

	Page
Introduction	7
Experimental Methods	8
Results and Discussion	10
Sodium-Potassium Nitrate	10
Lithium-Sodium-Potassium Nitrate	14
Summary	18
References	19

ILLUSTRATIONS

	Page
Figure 1. Depth of penetration profile for copper radiation in NaFeO ₂ , calculated at 2θ=40 degrees	9
Figure 2. X-ray diffraction spectra for corroded Alloy 800 indicating the occurrence of product phases at successive sections	11
Figure 3. Electron microprobe analysis of elemental concentration profiles in corroded Alloy 800 corresponding to Fig. 2 (a) Fe, Cr, Ni, Na (b) O, N	12
Figure 4. Surface cross-section micrograph of Alloy 800 indicating phase identifications of corrosion products	13
Figure 5. Surface cross-section micrograph of Type 316 Stainless Steel indicating phase identifications of corrosion products	15
Figure 6. X-ray diffraction spectra of Alloy 800 following contact with a lithium-containing nitrate salt illustrating the ordering of corrosion product phases observed at successive sections	16
Figure 7. Surface cross-section micrograph of Alloy 800 after contact with lithium-containing salt indicating phase identifications	17

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Introduction

X-ray diffraction analysis is the primary method of identifying chemical compounds in the solid state formed as a result of high temperature corrosion processes [1]. Recent developments in the areas of Raman spectroscopy [2,3] and Fourier transform infrared reflectance spectroscopy [4] show considerable promise for compound analysis, but an encyclopedic database of standards similar to that compiled for x-ray patterns is not yet available. Other methods of chemical identification, such as electron microprobe analysis and scanning Auger microscopy, are limited to elemental analyses, but provide useful information for corroborating phase identifications made by x-ray diffraction, as well as detecting solid solutions.

This report concerns the use of x-ray diffraction techniques to identify corrosion products formed on Fe-Ni-Cr alloys after immersion in molten alkali nitrate salts. Corrosion experiments were conducted as part of a program to evaluate structural materials for solar central receiver systems, operating at temperatures of 300°C to 600°C, which use molten nitrate salts as the heat transfer and storage medium[5]. The salt mixture of primary interest in this study was NaNO₃-KNO₃ since it has been used in large-scale receiver prototype tests[6]. Preliminary studies of Alloy 800 and Type 316SS test specimens immersed in this salt for several thousand hours revealed that complex, multilayered corrosion products were formed and that a transition in the corrosion rate occurred at a temperature of about 600°C, which resulted in accelerated corrosion[7]. One goal of this study was to determine the corrosion products formed above the transition temperature which led to accelerated corrosion.

Identification and spatial resolution of the chemical compounds in each layer of the corrosion scale required analysis of test specimens in the as-formed state. However, the total thickness of the corrosion products exceeded 25 microns in most cases, which is much too thick to allow penetration of the entire layer by available radiation sources. By adopting a step-wise procedure of analysis, which is described in the following pages, accurate phase identifications were possible without altering the spatial sequence of the corrosion products. Step-wise x-ray diffraction analysis has been used previously in less complex systems to study multiphase products resulting from high temperature oxidation of hafnium [8] and zirconium [9] and sulfidation of copper alloys [10].

The technique of x-ray diffraction with step-wise sectioning was also used in an ancillary study involving corrosion of Alloy 800 in the

ternary salt mixture, $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$. It was speculated that a protective layer of LiCrO_2 might be formed in this salt, based on reports of the behavior of similar alloys in the eutectic $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ salt mixture [11]. Such a layer might be more protective at the highest anticipated temperatures, or during over-temperature conditions, than the products formed in $\text{NaNO}_3\text{-KNO}_3$. Since no other surface characterization techniques were able to detect Li-containing compounds, x-ray diffraction analysis was essential for this part of the study.

Experimental Methods

The alloys examined in this study were Alloy 800 (Fe-32Ni-20.5Cr, minor Mn,Ti,Al,Si,Cu) and Type 316 Stainless Steel (Fe-18Cr-12Ni-2Mo, minor Mn,Si) which were fabricated into coupons with dimensions of 12 mm x18 mm x1.5 mm thick. Surface preparation was by grinding with 180 grit SiC paper after which coupons were immersed in melts of reagent grade salt mixtures in contact with air. Alloy 800 and Type 316SS were immersed in $\text{NaNO}_3\text{-KNO}_3$ (1:1 molar) for 2008 hours at 630°C . Alloy 800 was also tested in $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$ (1:1:1 molar) at 615°C for 1028 hours.

Corroded coupons were analyzed using an automated Diano diffractometer equipped with a Cu-targeted x-ray tube. The diffractometer operated in digital scan mode scanning $10^\circ\text{-}80^\circ 2\theta$ at $1.6^\circ/\text{min}$ with counts recorded every 1.6 seconds ($\Delta 2\theta = 0.04^\circ$). Data was collected by a DEC 11-34 computer system with output to a Tektronix-4014 terminal where the data was plotted using the SPEC PLOT program [12]. Product phases were identified by manual comparison with the JCPDS standard file.

The effective depth of x-ray penetration can be calculated using

$$G_x = 1 - \exp(-2\mu x / \sin(\theta))$$

where G_x is equal to the fraction of the total diffracted intensity which is contributed by a surface layer of depth x , μ is the linear absorption coefficient, and θ is the diffraction angle for which the calculation is made [13]. Using a diffractometer value of $2\theta = 40^\circ$, the midpoint of the scanning range used, a graphical illustration of G_x vs. penetration depth, x , can be constructed. Initial x-ray analyses of the near-surface portion of the corrosion layer on Alloy 800 and 316SS specimens identified NaFeO_2 as the major phase present and NiO as the minor phase. Figure 1 shows that 50 percent of the diffracted intensity originates from a depth of 2 microns and that 95 percent of the diffracted intensity is derived from a depth of up to 7 microns, substantially less than the 25 micron thickness of the corrosion layer. Therefore, initial x-ray analysis of the specimens only provides information from the surface portions of the oxide scale.

A sectioning technique was employed to progressively remove layers of oxide scale by lightly sanding the specimen on 600 grit carborundum

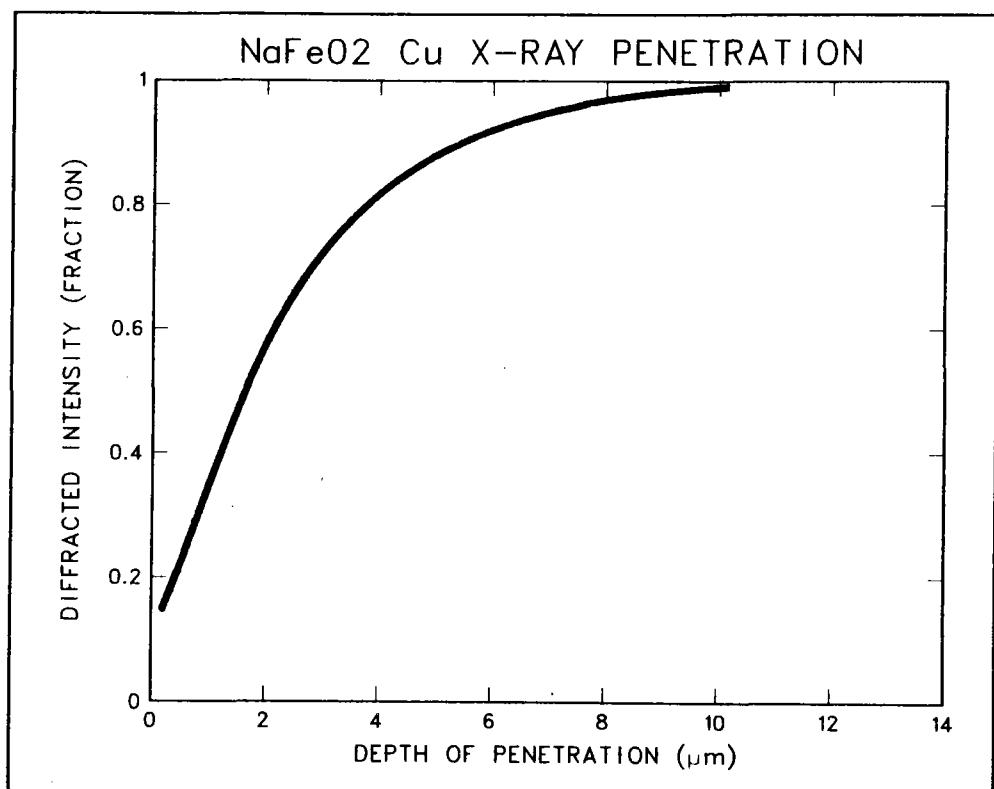


Figure 1. Depth of penetration profile for copper radiation in NaFeO_2 , calculated at $2\phi=40$ degrees.

paper. This procedure was accomplished in several steps with x-ray analysis performed at each successive step, thus providing diffraction information for the entire depth of scale thickness. This method enabled spatial resolution of the chemical phases in the scale in the as-formed condition as opposed to removing the scale by chemical or mechanical methods and homogenizing the sample for analysis.

Results and Discussion

Sodium-Potassium Nitrate

X-ray diffraction analysis of Alloy 800 (630°C , 2008 hours) at numerous intervals during the sectioning process revealed six distinct phases resulting from the corrosion process, as shown by the x-ray diffraction spectra in Figure 2. The surface of the corrosion layer, before any material was removed, was composed primarily of NaFeO_2 , although NiO was detected as a minor phase. The NiO phase disappeared upon removal of a small amount of the corrosion scale and successive sections resulted in increases in intensity of an Fe_3O_4 spinel (magnetite) phase. Further removal of material revealed progressive increases in intensity, followed by declines, for the rhombohedral oxide, Cr_2O_3 , elemental Ni, and CrN . Subsequent sectioning revealed only the diffraction spectra of the base alloy.

The results of x-ray diffraction analysis were supplemented by electron microprobe analysis of metallographically prepared cross-sections of the same sample. In Figure 3(a) and 3(b), elemental concentration profiles of the metallic elements, Cr, Fe, Ni, Na and the oxidants, O and N, are plotted respectively. These plots indicate the relative elemental compositional variations within each phase. The data is necessarily semi-quantitative due to the unavailability of individual oxide standards.

The electron microprobe data demonstrate that both the spinel and rhombohedral oxide phases identified by x-ray diffraction are composed of more than a single metal. The spinel phase, designated Fe_3O_4 above, had a minimum Fe:Cr ratio of four or five to one, and a Cr concentration gradient was observed which decreased outward, as shown in figure 3(a). Since Cr^{+3} may be incorporated into magnetite on the octahedral sites ordinarily occupied by Fe^{+3} , this implies a solid solution spinel oxide with the approximate composition, $\text{Fe}(\text{Fe}_{1.5}\text{Cr}_{.5})\text{O}_4$, and lesser amounts of Cr[14]. Similarly, the rhombohedral oxide phase, with the Cr_2O_3 structure indicated by x-ray diffraction, had a Cr:Fe ratio of roughly 3:1. Since Fe_2O_3 is completely miscible in Cr_2O_3 in all proportions, a solid solution oxide having the approximate composition, $\text{Cr}_{1.5}\text{Fe}_{.5}\text{O}_3$ is implied[15]. The variation in lattice parameter due to the substitution of Fe^{+3} for Cr^{+3} was not resolvable in the diffraction spectra acquired in this study[16].

Combining the information from sequential x-ray diffraction spectra with electron microprobe scans, the spatial organization of the corrosion products was determined, as shown in Figure 4. NiO was present as isolated

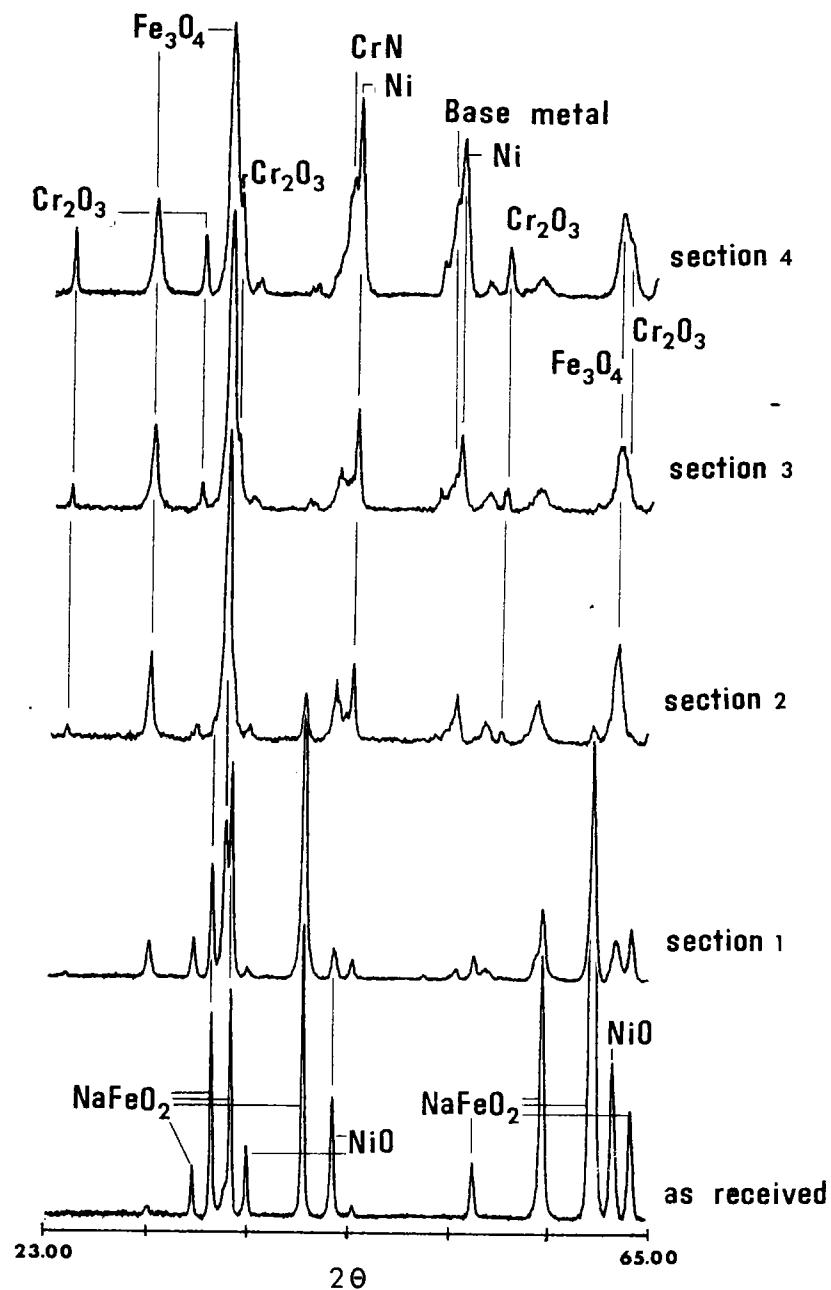


Figure 2. X-ray diffraction spectra for corroded Alloy 800 indicating the occurrence of product phases at successive sections.

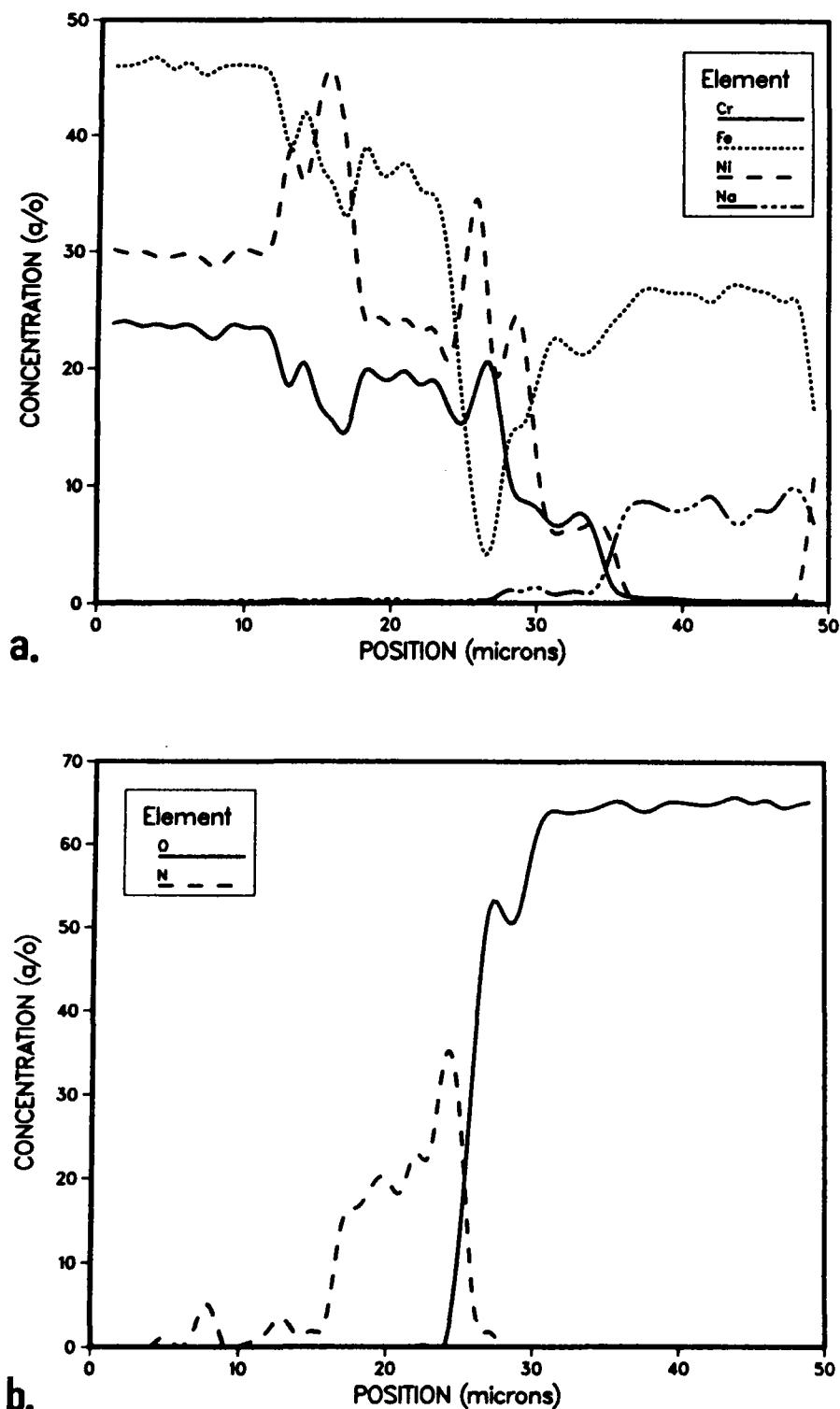
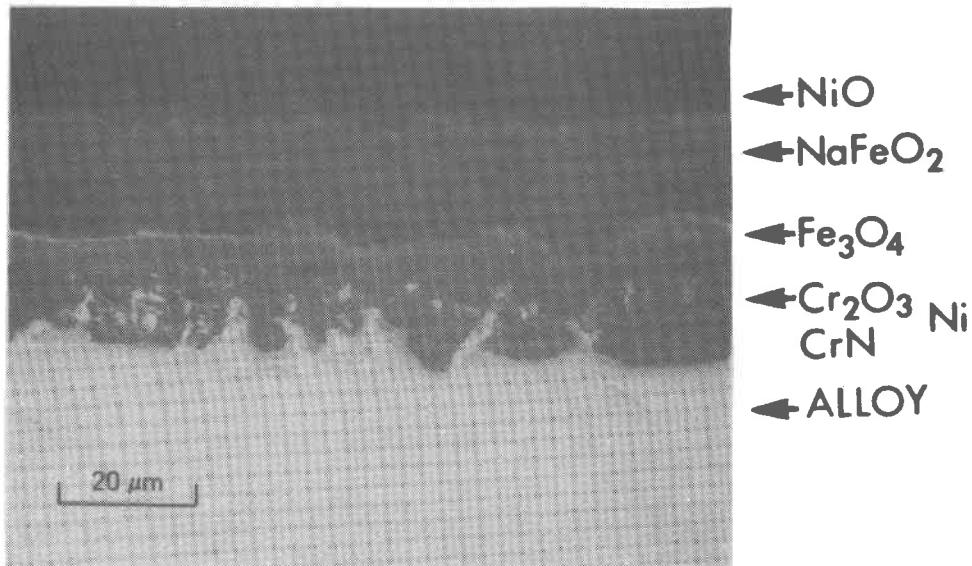


Figure 3. Electron microprobe analysis of elemental concentration profiles in corroded Alloy 800 corresponding to Fig. 2
 (a) Fe, Cr, Ni, Na
 (b) O, N



IN 800 630°C 2008 Hrs

Figure 4. Surface cross-section micrograph of Alloy 800 indicating phase identifications of corrosion products.

crystallites embedded in the outer(salt-contacting) surface of an NaFeO_2 layer approximately 12-14 microns thick. Beneath this was a layer of oxide with the Fe_3O_4 structure, about 6-8 microns deep, containing some Cr^{+3} in solid solution. Further in towards the metal, a band containing a much thinner (2-3 microns) layer with the Cr_2O_3 structure, with Fe^{+3} in solid solution, and segregated precipitates of elemental Ni were observed. Finally, internally precipitated CrN was found.

X-ray diffraction analysis of a Type 316 stainless steel sample which was also immersed in molten $\text{NaNO}_3\text{-KNO}_3$ at 630°C for 2008 hours determined the corrosion product phases shown in Figure 5. The major phases found on Alloy 800, NaFeO_2 , Fe_3O_4 and Cr_2O_3 , were also found on 316SS, arranged in the same structural order. The oxides, Fe_3O_4 and Cr_2O_3 , were solid solutions similar to those described for Alloy 800. However, no NiO or elemental Ni was found, presumably because the relatively low Ni content of 316SS did not exceed the solubility limits of the various phases present in which Ni was found. No internal nitridation of 316SS was detected.

Lithium-Sodium-Potassium Nitrate

X-ray diffraction analysis was also used for analyzing corrosion products formed in $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$ salt mixtures. The corrosion product phase analyses obtained at various levels during the sectioning process are shown by the x-ray diffraction spectra in Figure 6 for a sample of Alloy 800 tested for 1028 hours at 615°C in the ternary salt. A major difference in the chemistry of the corrosion products was the replacement of the double oxide, LiFeO_2 , for NaFeO_2 as the outermost layer, as shown in the photomicrograph in Figure 7. This information was obtainable only by x-ray diffraction since Li or its compounds are not detectable by the other surface analysis techniques available, such as the electron microprobe. The corrosion layers underlying the LiFeO_2 layer were found to be quite similar to those observed in the binary salt. A layer of Fe_3O_4 , containing some Cr as before, covered a layer of Cr_2O_3 , which also contained some Fe. The latter compound was not as continuous as the Fe_3O_4 layer. Scattered islands of precipitated elemental Ni were also observed at the interface with the base alloy. No internal nitrides were detected.

LiCrO_2 was not observed as a corrosion product following immersion in the ternary salt, just as NaCrO_2 was not found in the binary salt. The absence of chromite compounds is probably a result of the high solubility of chromate and dichromate in nitrate melts [16] and the strong Lux-Flood basicity of the nitrate ion, which stabilizes the hexavalent state of chromium in the melt [17]. As expected given the similarity of the corrosion products, the corrosion rate of Alloy 800 was not materially reduced in $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$ compared to the binary salt at 615°C . At 630°C , the outer layer of corrosion products formed in the ternary salt were extremely fragile and were not recovered intact for analysis.

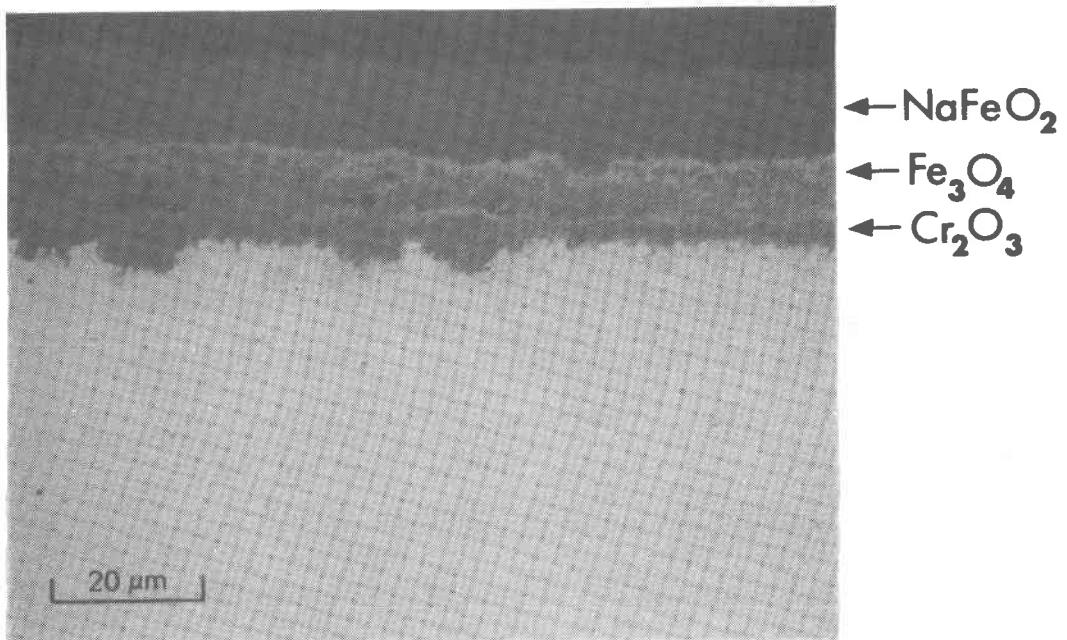


Figure 5. Surface cross-section micrograph of Type 316 Stainless Steel indicating phase identifications of corrosion products.

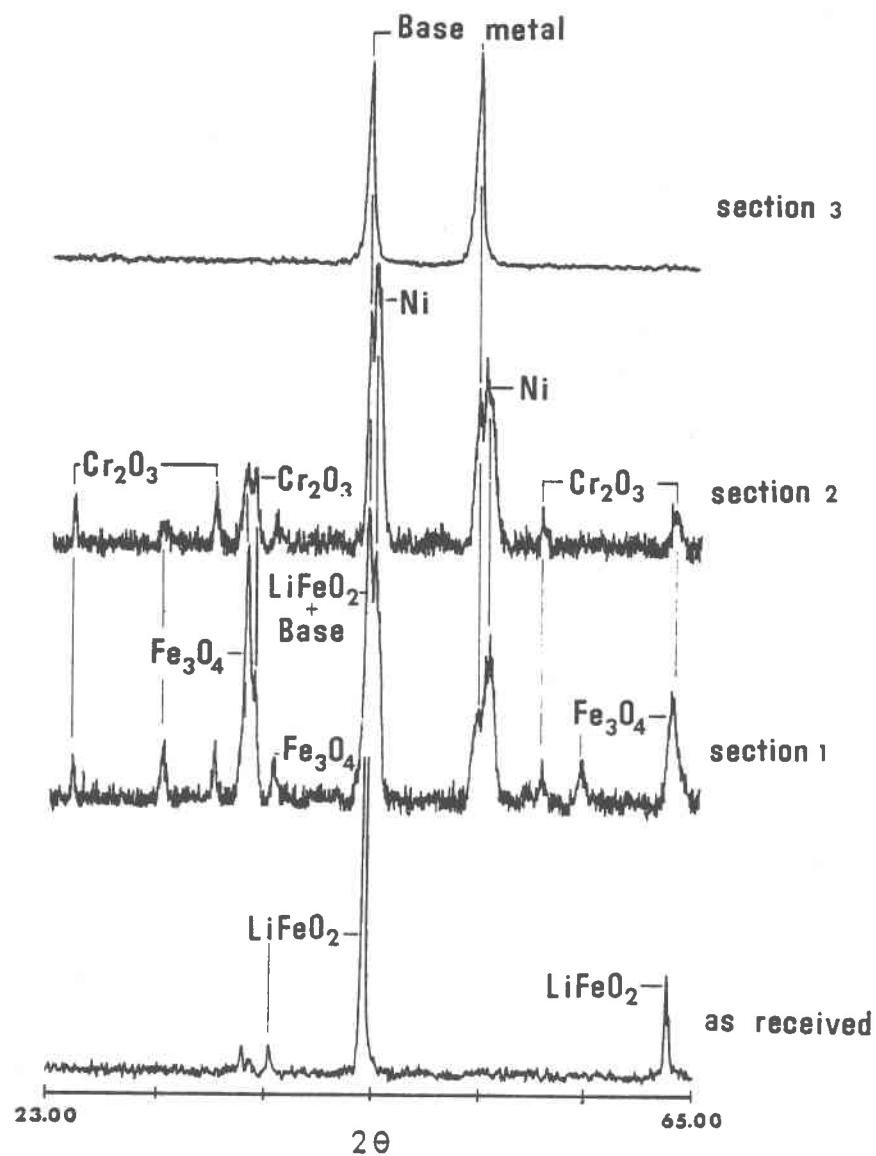


Figure 6. X-ray diffraction spectra of Alloy 800 following contact with a lithium-containing nitrate salt illustrating the ordering of corrosion product phases observed at successive sections.

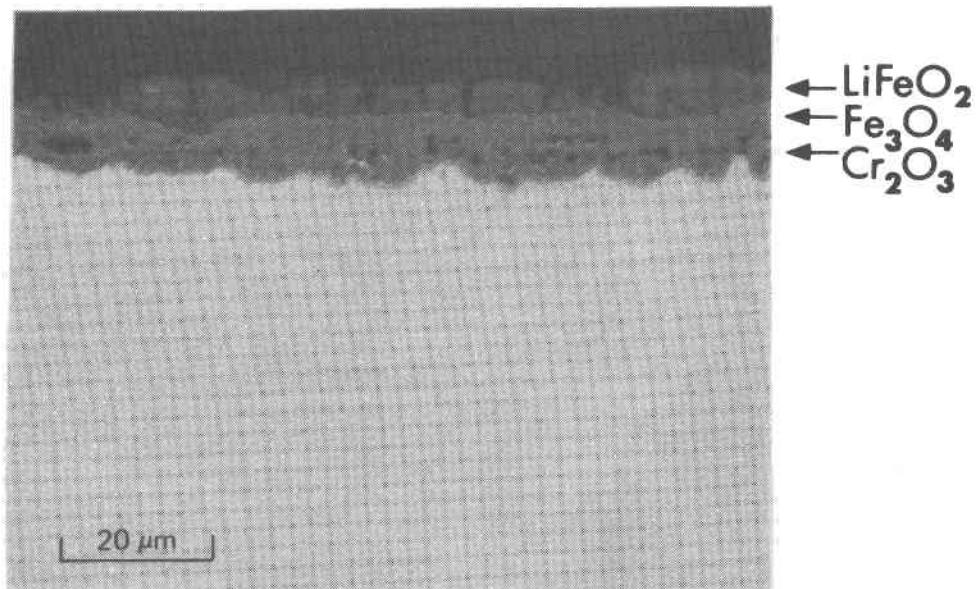


Figure 7. Surface cross-section micrograph of Alloy 800 after contact with lithium-containing salt indicating phase identifications.

Summary

X-ray diffraction was used to identify corrosion product phases formed on Alloy 800 and Type 316 stainless steel after prolonged contact with molten alkali nitrate salts. A sanding technique for serially sectioning surface corrosion layers provided an effective method of obtaining depth profiles of chemical compounds in thick, multilayered corrosion morphologies. The x-ray diffraction analyses were corroborated by electron microprobe scans and proved especially valuable for identifying oxides containing lithium, which were not detectable by other surface analysis techniques available.

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