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LOCALIZED CORROSION OF CANDIDATE CONTAINER MATERIALS IN FERRIC CHLORIDE SOLUTIONS*

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ABSTRACT

Localized corrosion behavior of candidate inner and outer container materials of currently-designed nuclear waste package was evaluated in aqueous solutions of various concentrations of ferric chloride ($FeCl_3$) at 30°C, 60°C and 90°C using the electrochemical cyclic potentiodynamic polarization (CPP) technique. Materials tested include A 516 carbon steel and high-performance alloys 825, G-3, G-30, C-4, 625, C-22, and Ti Gr-12. A 516 steel suffered from severe general and localized attack including pitting and crevice corrosion. High-nickel alloys 825 and G-3 also became susceptible to severe pitting and crevice corrosion. The extent of localized attack was less pronounced in alloys G-30 and C-4. Alloy 625 experienced severe surface degradation including general corrosion, crevice corrosion and intergranular attack. In contrast, only a slight crevice corrosion tendency was observed with nickel-base alloy C-22 in solutions containing higher concentrations of $FeCl_3$ at 60°C and 90°C. Ti Gr-12 was immune to localized attack in all tested environments. The test solutions showed significant amount of precipitated particles during and after testing especially at higher temperatures.

Keywords: Carbon steel, nickel-rich and nickel-base alloys, titanium alloy, ferric chloride solutions, temperature effect, electrochemical polarization, general corrosion, pitting and crevice corrosion.

INTRODUCTION

The high-level nuclear waste package designed during the current viability assessment (VA) period is focused on all-metallic multi-barrier concepts to accommodate the nation's spent nuclear fuel and vitrified defense high-level nuclear waste for geologic disposal in the potential Yucca Mountain repository. This design incorporates a thick outer corrosion-allowance metal barrier over a thinner inner container made of suitable corrosion-resistant alloy. The outer container is intended to provide galvanic protection to the inner container from the potential repository environment should the former be breached.

* $FeCl_3$ concentratioins used in this study are to be construed as the initial concentrations.

The results[1,2] of numerous electrochemical corrosion studies previously performed at the Lawrence Livermore National Laboratory (LLNL) involving several candidate inner-container waste package materials have shown that alloy C-22 and Ti Gr-12 were immune to localized attack in sodium chloride-containing aqueous environments of various pHs at temperatures up to 90°C. Since A 516 steel is the primary candidate material for the outer containment barrier in the VA design of the waste package it is possible that the inner container material may come in contact with aqueous solutions containing ferrous/ferric ions (Fe^{+2}/Fe^{+3}) resulting from the dissolution of A 516 steel. Furthermore, these ions may react with chloride ions present in the near-field environment, thus leading to the formation of aggressive salts such as ferric chloride ($FeCl_3$). In view of this scenario, additional electrochemical polarization experiments were recently performed at LLNL on both candidate inner and outer container materials in aqueous environments containing various concentrations of $FeCl_3$ at different temperatures. This paper presents the test results showing the effects of temperature and $FeCl_3$ concentration on the electrochemical corrosion behavior of these alloys.

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials tested include iron-nickel-chromium-molybdenum (Fe-Ni-Cr-Mo) alloys 825, G-3 and G-30; Ni-Cr-Mo alloys C-4, 625 and C-22; titanium (Ti)-base alloy Ti Gr-12; and A 516 steel. Their chemical compositions are given in Table 1. The cylindrical specimens were fabricated from heat-treated plate materials by a qualified vendor and additional thermal treatments were not given to these specimens prior to their exposure to the test environments.

A three-electrode technique was used to perform CPP experiments in a Pyrex cell using a cylindrical test specimen as working electrode, two graphite counter electrodes, and a Luggin capillary connected to a Ag/AgCl reference electrode. The test specimens were polished with 600-grit paper and cleaned with distilled water prior to their exposure to the test solutions. Electrochemical potential was applied to the test specimens at a scan rate of 0.17 mV/sec using EG&G Models 273 and 283 potentiostats, controlled by an IBM-compatible PC with EG&G corrosion software. The relevant experimental details have been described elsewhere.[1]

Tests were performed in deaerated aqueous solutions initially containing 0.6-4.0 weight percent (wt%) $FeCl_3$ at temperatures of 30°C, 60°C and 90°C. The pH of the test solution was measured at room temperature prior to initiation of each experiment. The pH of these test solutions ranged between 1.60 and 2.20, the pH becoming more acidic with increased $FeCl_3$ concentration. At the conclusion of each test the specimen was cleaned with distilled water. The cleaned specimen was visually examined followed by an optical microscopic evaluation to detect the presence or absence of different forms of localized attack. Scanning electron microscopy (SEM) and energy dispersive spectroscopic (EDS) analyses were performed on a few selected test specimens to detect and identify chemical species present in different areas of the degraded surface of the tested specimen.

RESULTS AND DISCUSSION

Results indicate that A 516 steel underwent severe general and localized corrosion. The severity of attack was more pronounced in solutions containing higher concentrations of $FeCl_3$ at 90°C. Alloys 825 and G-3 also became susceptible to severe pitting and crevice corrosion. Surface degradation including intergranular attack was observed in these two alloys particularly in solutions containing higher concentrations of $FeCl_3$ at 90°C. The extent of localized attack was less severe with alloys G-30 and C-4. Intergranular attack was observed with alloy 625 that also suffered from general corrosion and crevice corrosion in environments initially containing 3.05-4.0 wt% $FeCl_3$ at higher test temperatures. As to the localized corrosion behavior of Alloy C-22, only slight crevice corrosion was observed in solutions containing higher concentrations of $FeCl_3$ at 60° and 90°C. In other environments alloy C-22 specimens were stained to some extent. Neither pitting nor crevice corrosion was observed with Ti Gr-12 in any environments tested. A macroscopic view of specimens tested in an aqueous solution of 4 wt% $FeCl_3$ at 90°C is shown in Figure 1.

It is well known[3] that the initiation of crevice corrosion in metallic materials immersed in chloride-containing aqueous environments may involve the dissolution of metal and maintenance of a high degree of acidity within the crevice solution by the hydrolysis of the dissolved metal ions. The acid produced by the hydrolysis reaction keeps the pH to very low values, while the pH of the solution outside the crevice remains more neutral. In simple terms, the electrolyte present within an actively corroding crevice may be regarded as concentrated hydrochloric acid containing metal chlorides dissolved at concentrations near saturation. An interesting observation made in this study was that the $FeCl_3$ solutions of various concentrations showed significant amount of precipitated particles upon completion of testing especially at temperatures of 60°C and 90°C. The final pH of the clear solution above the precipitated particles was still very acidic, as determined by occasional measurements. It is possible that the pH of crevice solutions for susceptible alloys may be even lower than that of the bulk solutions in which the test specimens were polarized at higher temperatures. The formation of precipitated particles during CPP experiments, particularly at higher temperatures may raise questions as to the validity of performing corrosion experiments in concentrated $FeCl_3$ solutions at temperatures at which these solutions may become unstable. One way of preventing precipitation and enhancing the reproducibility of test results is to add a complexing agent such as Na_2EDTA.$^{(4)}$ However, such addition of a complexing agent to $FeCl_3$ solutions may be inappropriate due to the lack of relevance to the potential repository environment for the waste package.

The initiation of pitting in susceptible active-passive metals and alloys is the result of the breakdown of the passive films on their surface in the presence of aggressive anions such as chloride ions (Cl^-), and the subsequent establishment of an electrochemical cell in which the damaged site acts as an anode and the surrounding passive surface acts as a cathode. The results$^{(1,2)}$ of previous CPP studies conducted in aqueous solutions of NaCl showed that the critical pitting potential (E_{pit}) for susceptible alloys was shifted to more active (negative) values with increasing Cl^- concentration. In contrast, the results of recent testing in $FeCl_3$ solutions indicate that the E_{pit} values for these alloys were more noble and did not change significantly due to changes in $FeCl_3$ concentration at different temperatures. Efforts were also made to correlate $FeCl_3$ concentration to the repassivation or protection potential (E_{prot}) values obtained from the CPP experiments. In majority of these tests the value of E_{prot} could not be determined since the return polarization curve did not intersect the forward polarization curve at the passive current density.

The critical potential at which slope change occurred in the forward polarization curves for Alloy C-22 and Ti Gr-12 in previous studies$^{(1,2)}$ was not significantly influenced by the variation of NaCl concentration. A similar behavior was observed in experiments performed in $FeCl_3$ solutions in that this critical potential was almost independent of the $FeCl_3$ concentration at various temperatures tested. However, the magnitude of this critical potential was slightly higher for Alloy C-22 in $FeCl_3$ solutions compared to those in NaCl environments. For Ti Gr-12 the critical potential values obtained in $FeCl_3$ solutions were very high and resembled those measured in NaCl solutions at similar temperatures. The excellent corrosion resistance of Ti Gr-12 in all tested environments is thought to be primarily due to the inert, tightly adherent protective oxide films that cover its surface.

An attempt was made to compare the open circuit or corrosion potential (E_{corr}) values of test materials in both NaCl and $FeCl_3$ solutions. Results indicate that for A 516 steel the measured E_{corr} values became more noble in $FeCl_3$ solutions compared to those in brines containing NaCl. For example, the E_{corr} value for this active material ranged between -740 and -563 mV in brines containing different concentrations of NaCl at various test temperatures. But the same material showed E_{corr} values ranging between -483 and -381 mV when tested in $FeCl_3$ solutions at similar temperatures, as illustrated in Figure 2. A similar ennoblement phenomenon of E_{corr} was observed for the Fe-Ni-Cr-Mo, Ni-Cr-Mo, and Ti alloys when tested in $FeCl_3$ solutions but the magnitude of potential shift in these alloys was significantly higher than that observed with A 516 steel. An important observation made from these analyses was that the E_{corr} value for Ti Gr-12 was shifted to much higher values in $FeCl_3$ solutions with increasing temperature as shown in Figure 3.

It has been suggested$^{(5,6)}$ that ferric ions (Fe^{+3}) may act as cathodic depolarizers and shift the corrosion potential of titanium alloys in the positive direction, a phenomenon which was also observed in this study. It is possible that the concentration of Fe^{+3} ions formed in a $FeCl_3$ solution may increase with an increase in temperature, thus resulting in a much larger shift in E_{corr} value in the noble direction for Ti Gr-12. A similar mechanism may possibly be attributed to the observed ennoblement of E_{corr} values for Fe-Ni-Cr-Mo and Ni-Cr-Mo alloys investigated.

Substantial effort was focused on SEM studies of alloys C-22 and 625 specimens polarized in acidic brines containing $FeCl_3$ and NaCl at 90°C. As indicated earlier, alloy 625 became susceptible to crevice corrosion and intergranular attack in solutions containing higher concentrations of $FeCl_3$ at elevated temperatures. Similar type of surface degradation was also observed$^{(2)}$ in alloy 625 when tested in acidic brines containing NaCl at 60°C and 90°C. On the contrary, alloy C-22 was immune to localized attack in NaCl solutions in the previous study$^{(2)}$ and showed only a slight crevice corrosion tendency in highly concentrated $FeCl_3$ solutions at 60°C and 90°C. The results of SEM study of polarized alloy 625 specimens are illustrated in Figures 4 and 5, showing intergranular attack in the creviced region. In contrast, either slight crevice corrosion or no attack was experienced by alloy C-22 as shown in Figures 6 and 7. Analyses of EDS spectra for alloy 625 revealed reduced concentration of both Ni and Cr and presence of Cl^- along the degraded surface area as shown in Figures 4 and 5. In addition, Nb and Mo concentration peaks were substantially higher in the same spectra. No chlorides were detected in the creviced region of alloy C-22.

The intergranular corrosion of alloy 625, as observed in this investigation, may be related to the sensitization phenomenon of high Ni-Cr-bearing alloys. It has been cited$^{(7,8)}$ that this type of preferential attack in alloy 625 may be associated with the precipitation of Cr and Mo-rich carbides of the type $M_{23}C_6$ and M_6C which may deplete the austenitic matrix of these elements in the vicinity of the grain boundaries. On the other hand, carbides of the M_6C type may be randomly distributed(2,7) throughout the austenitic matrix in alloy C-22 showing no apparent effect on corrosion resistance.

SUMMARY AND CONCLUSIONS

Electrochemical CPP technique was used to evaluate the localized corrosion susceptibility of candidate nuclear waste package container materials in deaerated aqueous environments initially containing 0.6, 1.0, 2.0, 3.05 and 4.0 wt% $FeCl_3$ at 30°C, 60°C and 90°C. Results obtained from these experiments were compared to previous data on similar materials tested in brines containing NaCl. SEM and EDS results were analyzed. The significant conclusions drawn from this study are given below:

- Severe general and localized corrosion were observed in A 516 steel. The extent of attack was more pronounced in the presence of increased $FeCl_3$ content at higher temperatures. The E_{corr} values became more noble compared to those in NaCl solutions at comparable test temperatures.

- Alloys 825, G-3, G-30 and C-4 became susceptible to pitting and crevice corrosion in all $FeCl_3$ environments tested. A similar localized corrosion behavior was also observed with these alloys when tested in brines containing NaCl but these alloys showed significantly more noble E_{corr} values in $FeCl_3$ solutions. The E_{pit} values of these alloys were not significantly influenced by the change in $FeCl_3$ concentration and test temperature contrary to the strong dependence of E_{pit} on these two variables in NaCl solutions.

- Alloys 825, G-3 and 625 experienced intergranular attack in solutions containing increased concentration of $FeCl_3$ at elevated temperatures. General corrosion and crevice corrosion were also observed with alloy 625 in these environments.

- Slight crevice corrosion tendency was observed with alloy C-22 in solutions containing higher concentrations of $FeCl_3$ at 60°C and 90°C but Ti Gr-12 was unattacked in all environments tested. The E_{corr} values for both alloy C-22 and Ti Gr-12 became more noble in $FeCl_3$ solutions compared to those in NaCl solutions. In addition, the E_{corr} value for Ti Gr-12 in $FeCl_3$ solutions was shifted to much higher values with increasing temperature, possibly due to the formation of increased Fe^{+3} which is known to cause ennoblement of E_{corr} for Ti and its alloys.

- The polarized alloy 625 specimens showed intergranular attack in the creviced area when tested in aqueous solutions containing either $FeCl_3$ or NaCl as evidenced by the SEM micrographs. EDS study of these specimens revealed reduced concentration of both Ni and Cr and presence of Cl^- along their degraded surface areas. No Cl^- ions were detected in the EDS spectra for alloy C-22 specimens polarized in similar environments.

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Table 1

Chemical Composition of Materials Tested (wt%)

Material	Lot #	C	Mn	P	S	Si	Ni	Cr	Mo	Fe	Ti	Al	Cu	Others
A 516 Steel	M060	0.15	0.70	0.014	0.003	0.20	0.19	0.17	0.05	Bal	--	0.021	0.30	Nb:0.002
Alloy 825	L703	0.02	0.50	--	0.002	0.50	39.10	19.50	2.60	34.80	1.00	0.06	1.70	--
Alloy G-3	K914	0.004	0.80	0.009	0.003	0.36	Bal	22.26	6.88	19.29	--	--	1.90	Nb+Ta:0.30 W:0.85
Alloy G-30	M049	0.01	1.10	0.01	<0.002	0.36	Bal	29.20	5.10	14.80	--	--	1.90	W:2.98
Alloy C-4	K991	0.004	0.16	0.006	0.006	0.02	Bal	15.68	15.49	0.25	0.21	--	--	Co:0.10
Alloy 625	L704	0.02	0.08	0.006	0.001	0.08	Bal	21.67	8.90	3.86	0.27	0.29	--	Nb+Ta:3.45
Alloy C-22	M048	0.003	0.19	0.009	0.005	0.024	Bal	21.19	13.36	4.12	--	--	--	W:2.97 V:0.14
Ti Gr-12	K270	0.0075	--	--	--	--	0.75	--	0.30	0.13	Bal	--	--	O:0.14 Y:<0.005

A 516 Steel

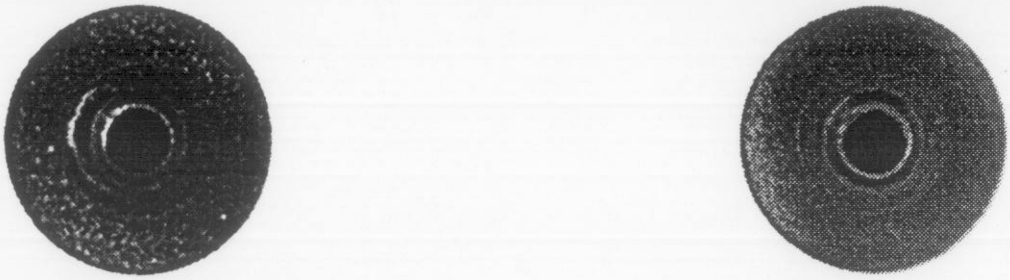
Alloy 825

Alloy G-3

Alloy G-30

Alloy C-4

Alloy 625



Alloy C-22

Ti Gr-12

Figure 1. Surface Appearance of Specimens Tested in Solutions Initially Containing 4 wt% $FeCl_3$ (pH ≈ 1.60) at 90°C

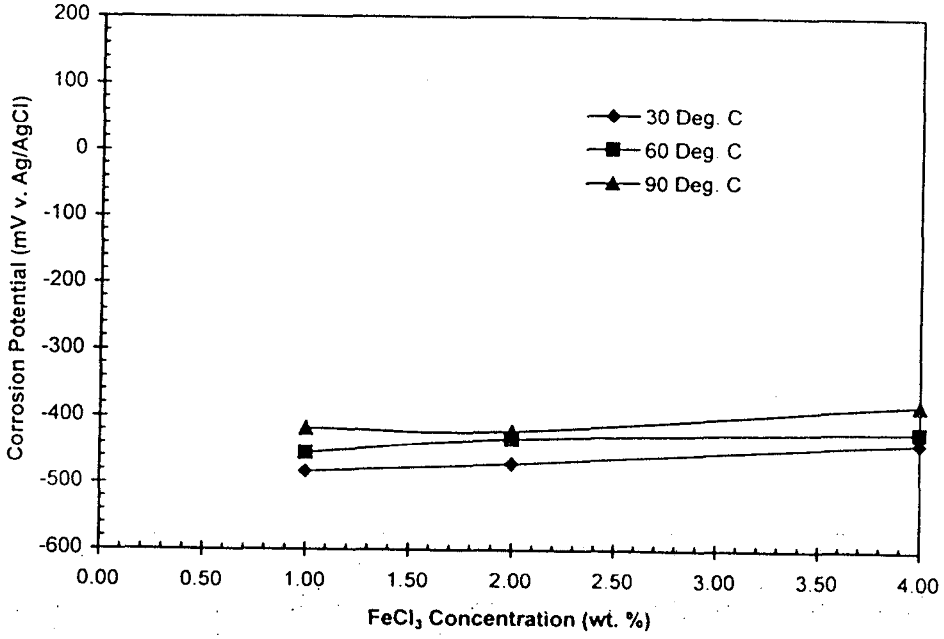


Figure 2. E_{corr} vs Initial $FeCl_3$ Concentration for A 516 Steel Tested at Different Temperatures

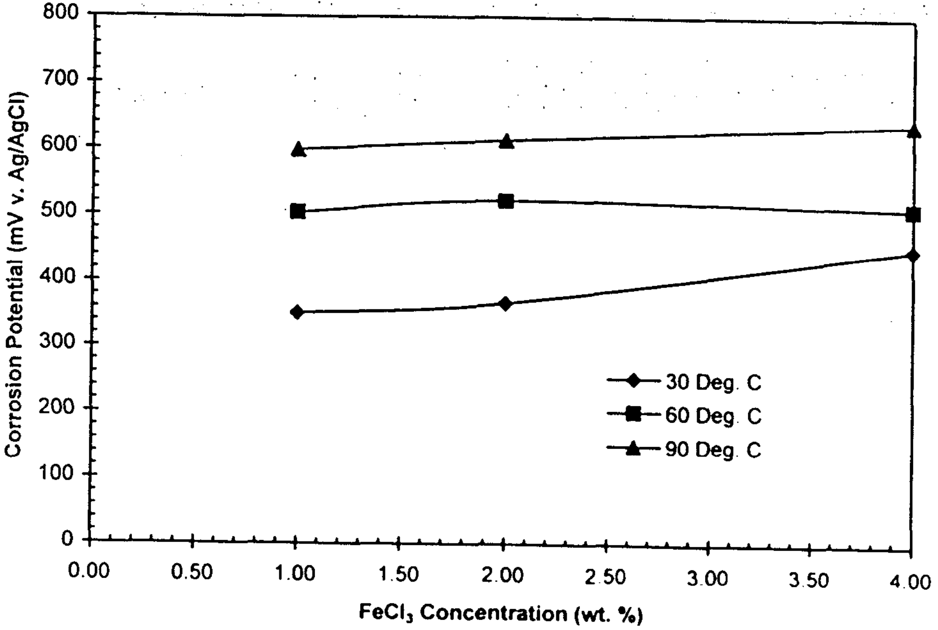


Figure 3. E_{corr} vs Initial $FeCl_3$ Concentration for Ti Gr-12 Tested at Different Temperatures

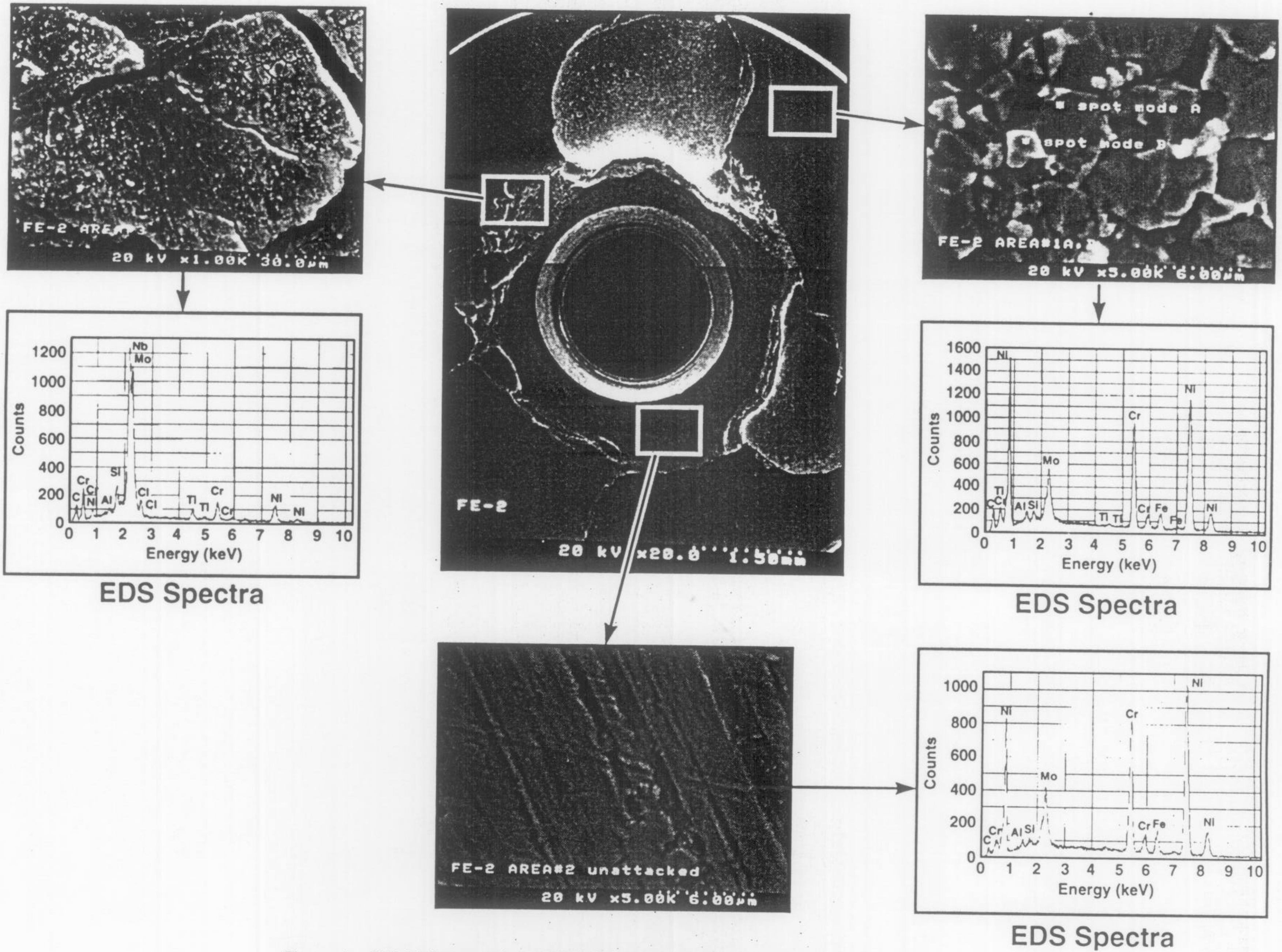


Figure 4. SEM Micrograph and EDS Spectra for Alloy 625 Specimen Polarized in Solution Initially Containing 3.05 wt% $FeCl_3$ (pH ≈ 1.72) at 90°C

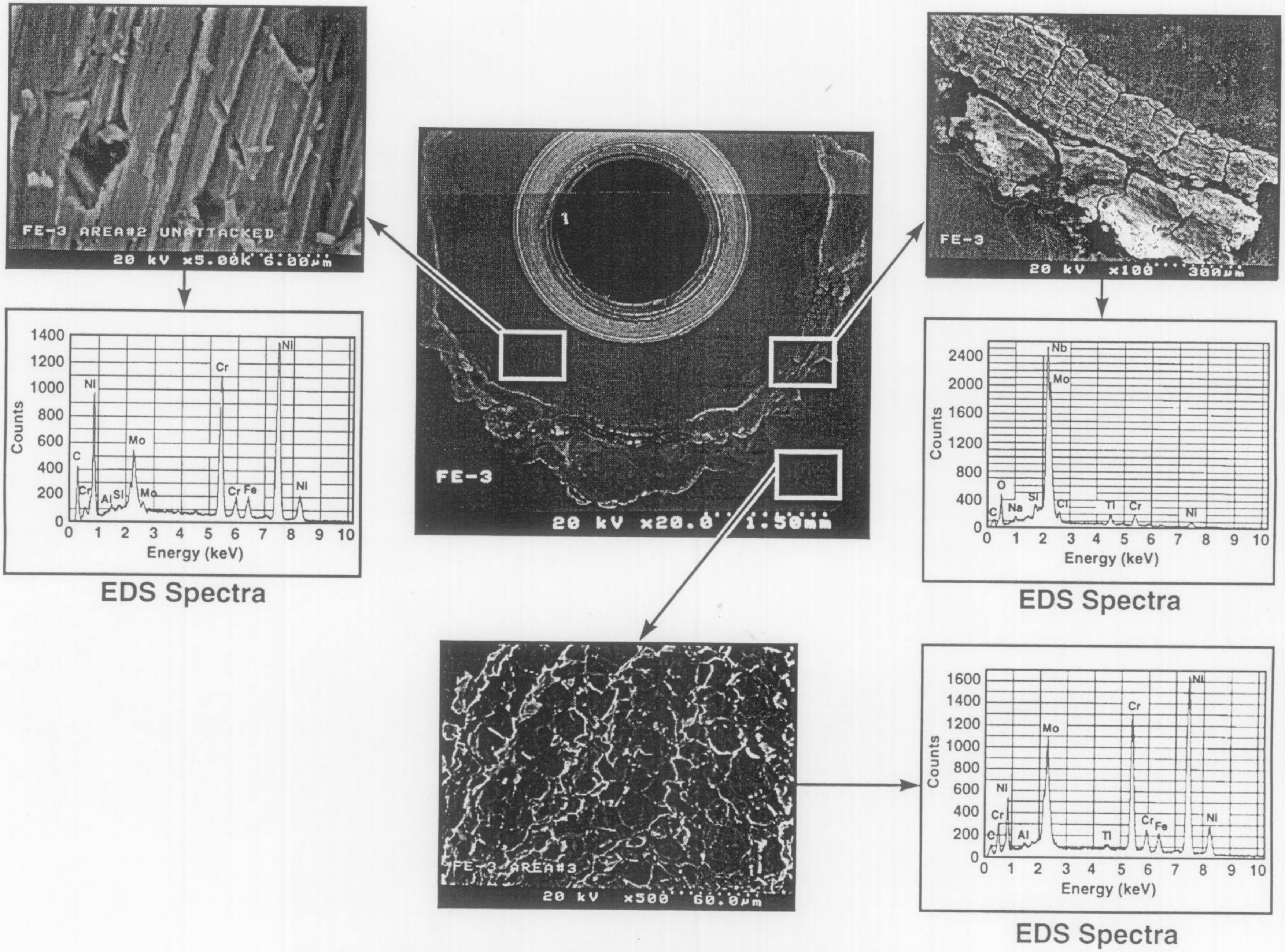


Figure 5. SEM Micrograph and EDS Spectra for Alloy 625 Specimen Polarized in Acidic Solution Containing 5 wt% NaCl (pH ≈ 2.69) at 90°C

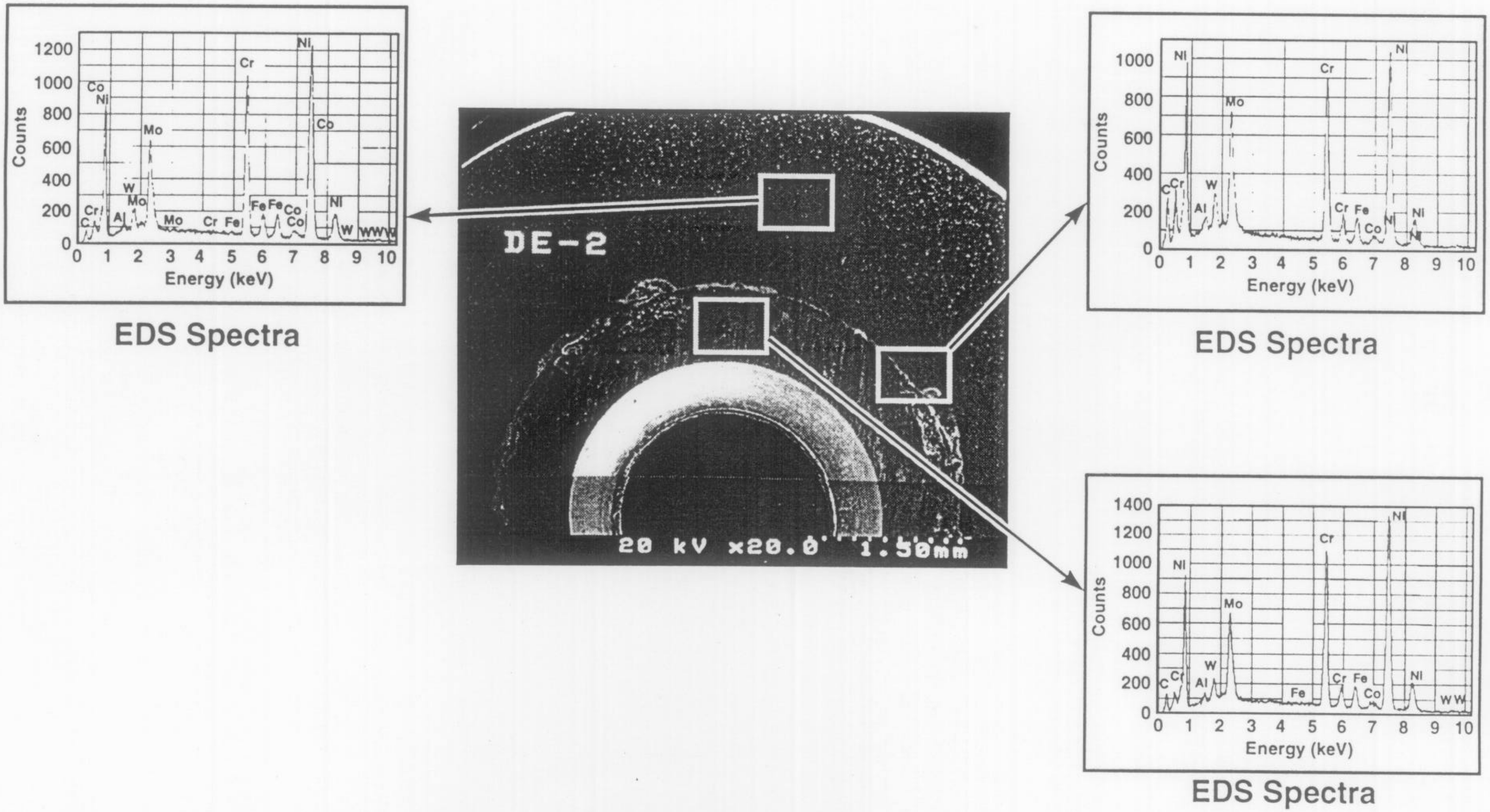


Figure 6. SEM Micrograph and EDS Spectra for Alloy C-22 Specimen Polarized in Solution Initially Containing 3.05 wt% $FeCl_3$ (pH ≈ 1.72) at 90°C

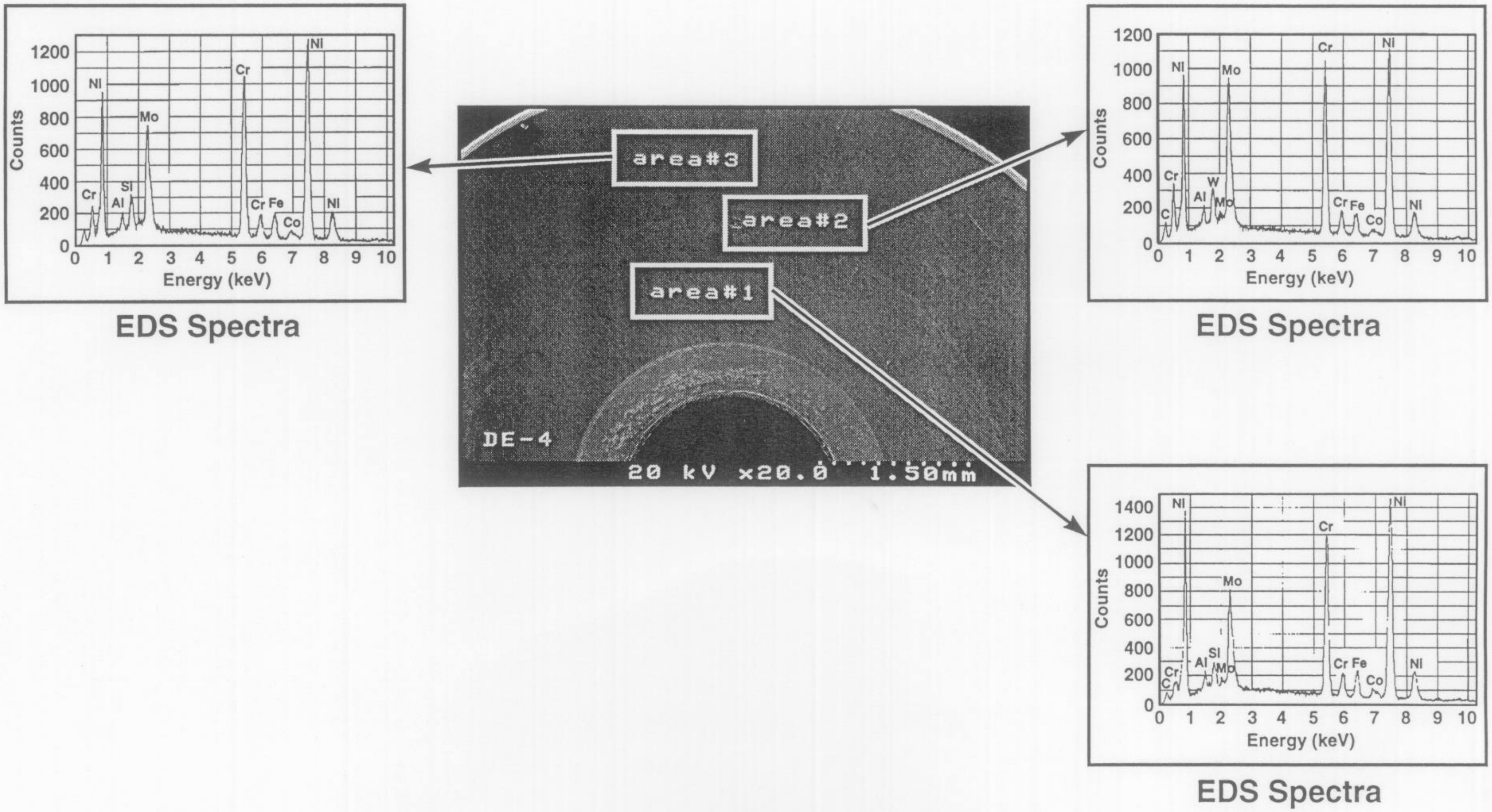


Figure 7. SEM Micrograph and EDS Spectra for Alloy C-22 Specimen Polarized in Acidic Solution Containing 5 wt% NaCl (pH ≈ 2.53) at 90°C