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C *Limited Metallurgical Examination*

C.1 Introduction

Two structural steel members with unusual erosion patterns were observed in the WTC debris field. The first appeared to be from WTC 7 and the second from either WTC 1 or WTC 2. Samples were taken from these beams and labeled Sample 1 and Sample 2, respectively. A metallurgic examination was conducted.

C.2 Sample 1 (From WTC 7)

Several regions in the section of the beam shown in Figures C-1 and C-2 were examined to determine microstructural changes that occurred in the A36 structural steel as a result of the events of September 11, 2001, and the subsequent fires. Although the exact location of this beam in the building was not known, the severe erosion found in several beams warranted further consideration. In this preliminary study, optical and scanning electron metallography techniques were used to examine the most severely eroded regions as exemplified in the metallurgical mount shown in Figure C-3. Evidence of a severe high temperature corrosion attack on the steel, including oxidation and sulfidation with subsequent intergranular melting, was readily visible in the near-surface microstructure. A liquid eutectic mixture containing primarily iron, oxygen, and sulfur formed during this hot corrosion attack on the steel. This sulfur-rich liquid penetrated preferentially down grain boundaries of the steel, severely weakening the



Figure C-1 Eroded A36 wide-flange beam.



Figure C-2
Closeup view of eroded wide-flange beam section.

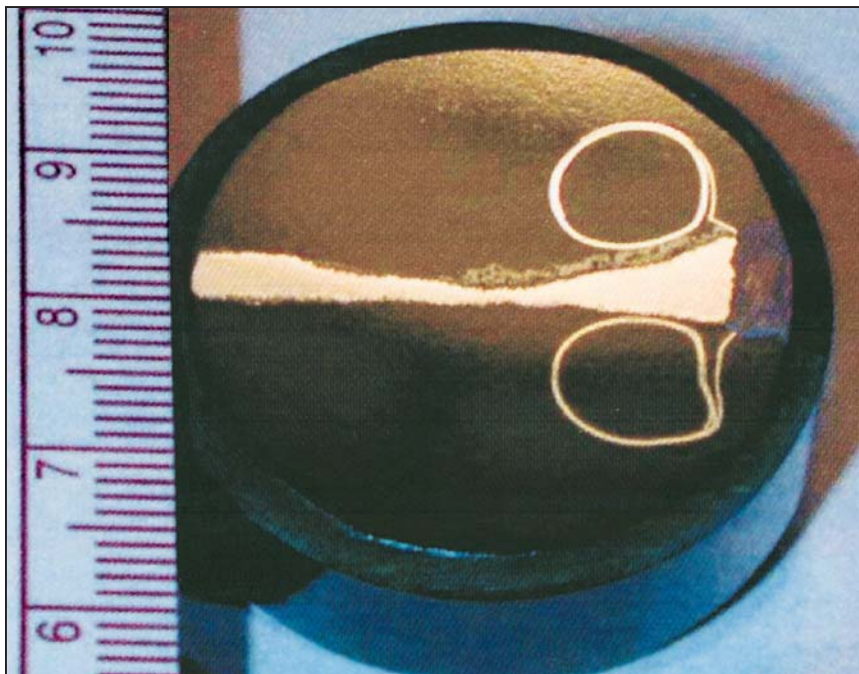


Figure C-3
Mounted and polished severely thinned section removed from the wide-flange beam shown in Figure C-1.

beam and making it susceptible to erosion. The eutectic temperature for this mixture strongly suggests that the temperatures in this region of the steel beam approached 1,000 °C (1,800 °F), which is substantially lower than would be expected for melting this steel.

When steel cools below the eutectic temperature, the liquid of eutectic composition transforms to two phases, iron oxide, FeO, and iron sulfide, FeS. The product of this eutectic reaction is a characteristic geometrical arrangement that is unique and is readily visible even in the unetched microstructure of the steel. Figures C-4 and C-5 present typical near-surface regions showing the microstructural changes that occur due to this corrosion attack. Figure C-6 presents the microstructure from the center of a much thicker

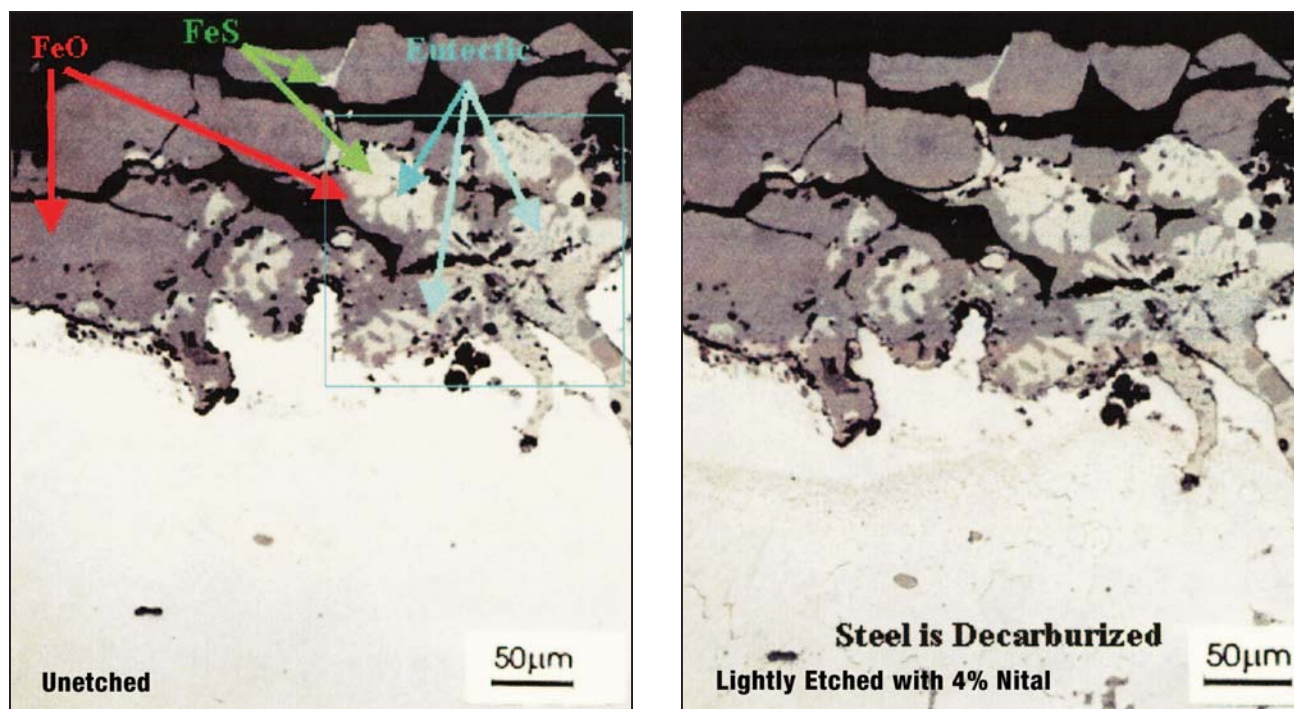


Figure C-4 Optical microstructure near the steel surface.

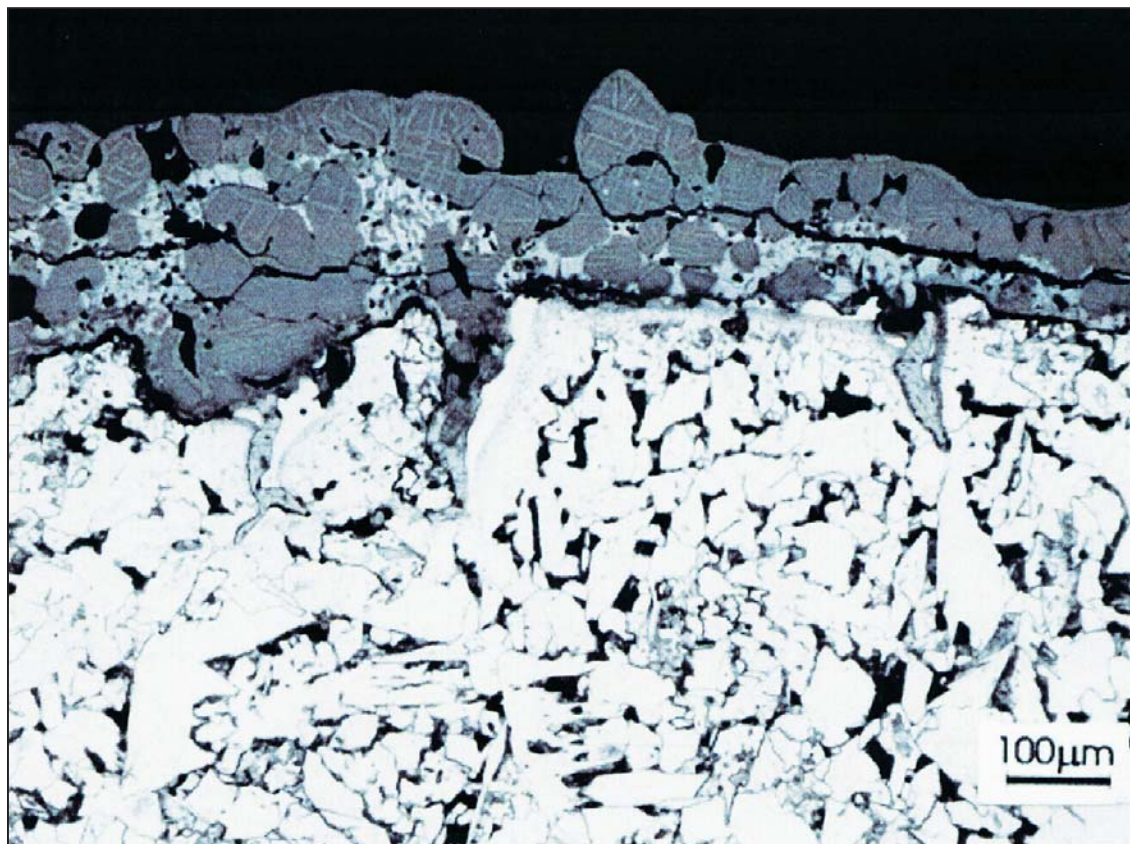


Figure C-5 Another hot corrosion region near the steel surface (etched with 4 percent nital). (Note: (1) Oxide rounding where the FeO-FeS eutectic product is present. (2) Reduction in banding of the steel when re-transformation occurs on cooling from austenite to ferrite and pearlite.)

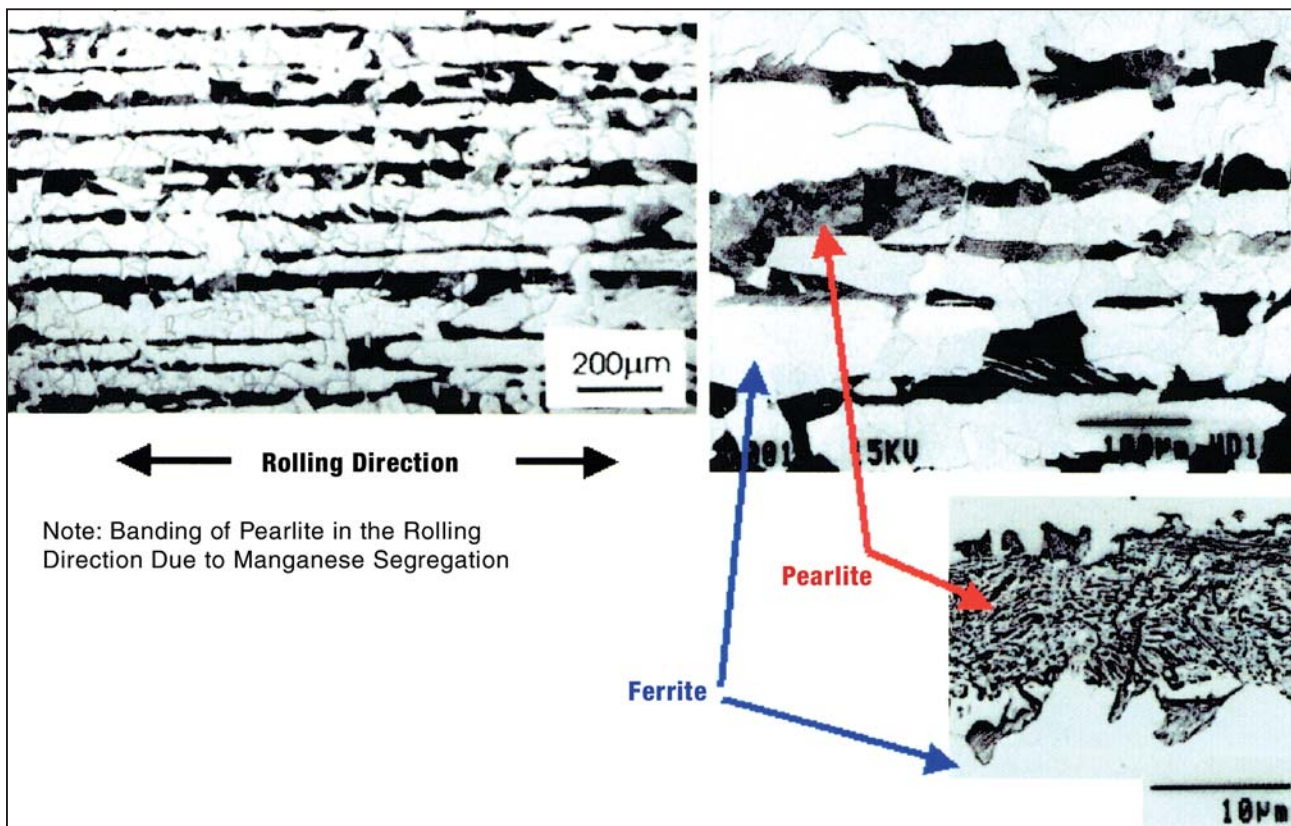


Figure C-6 Microstructure of A36 steel.

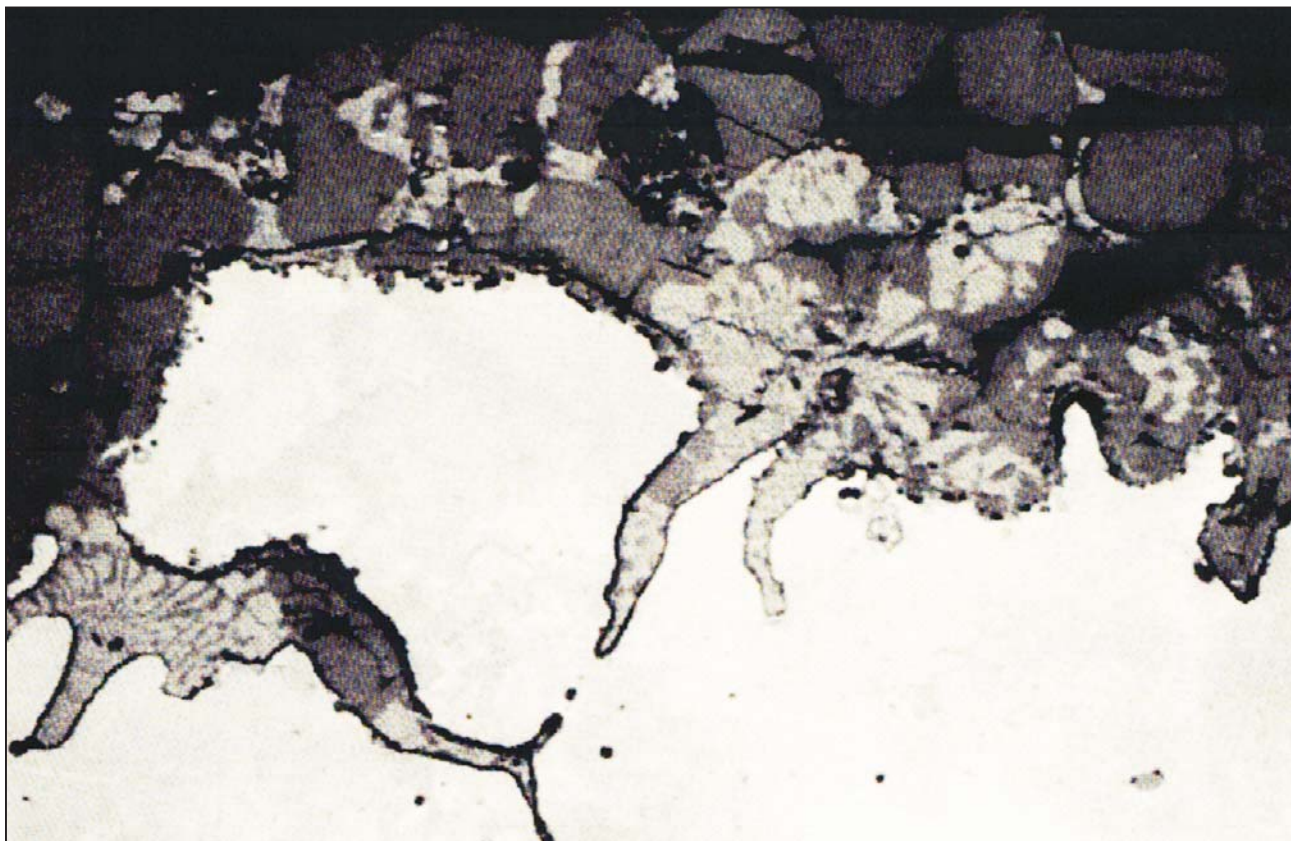


Figure C-7 Deep penetration of liquid into the steel. (Note: Hot corrosion of the steel can produce "islands" of steel surrounded by liquid, which will make erosion of the steel much easier.)

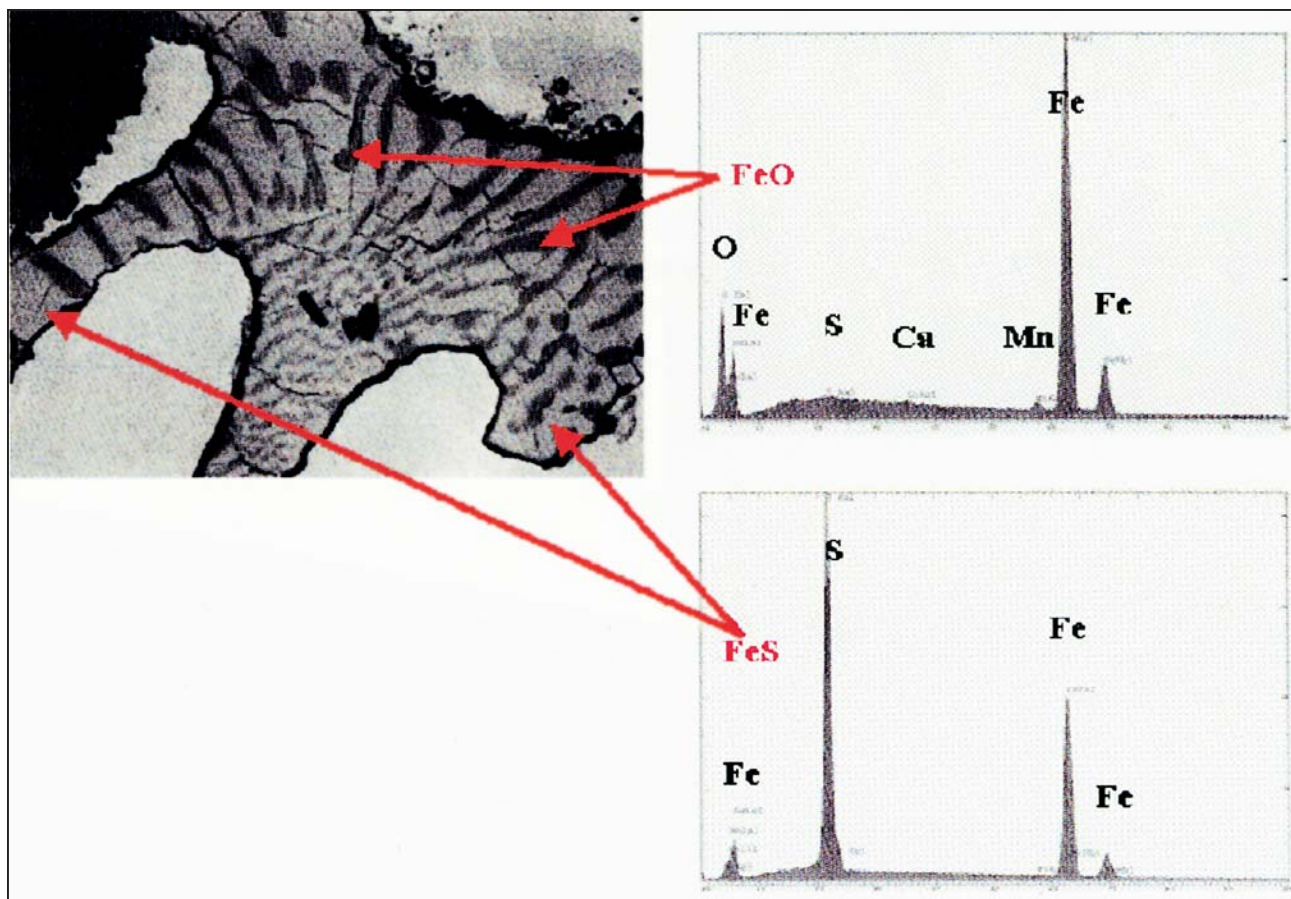


Figure C-8 Qualitative chemical analysis.

section of the steel that is unaffected by the hot corrosion. Figure C-7 illustrates the deep penetration of the liquid into the steel's structure. In order to identify the chemical composition of the eutectic, a qualitative chemical evaluation was done using energy dispersive X-ray analysis (EDX) of the eutectic reaction products. Figure C-8 illustrates the results of this analysis.

C.3 Summary for Sample 1

1. The thinning of the steel occurred by a high-temperature corrosion due to a combination of oxidation and sulfidation.
2. Heating of the steel into a hot corrosive environment approaching 1,000 °C (1,800 °F) results in the formation of a eutectic mixture of iron, oxygen, and sulfur that liquefied the steel.
3. The sulfidation attack of steel grain boundaries accelerated the corrosion and erosion of the steel.

C.4 Sample 2 (From WTC 1 or WTC 2)

The origin of the steel shown in Figure C-9 is thought to be a high-yield-strength steel removed from a column member. The steel is a high-strength low-alloy (HSLA) steel containing copper. The unusual thinning of the member is most likely due to an attack of the steel by grain boundary penetration of sulfur forming sulfides that contain both iron and copper. Figures C-10, C-11, and C-12 show the region of severe corrosion at different levels of magnification.

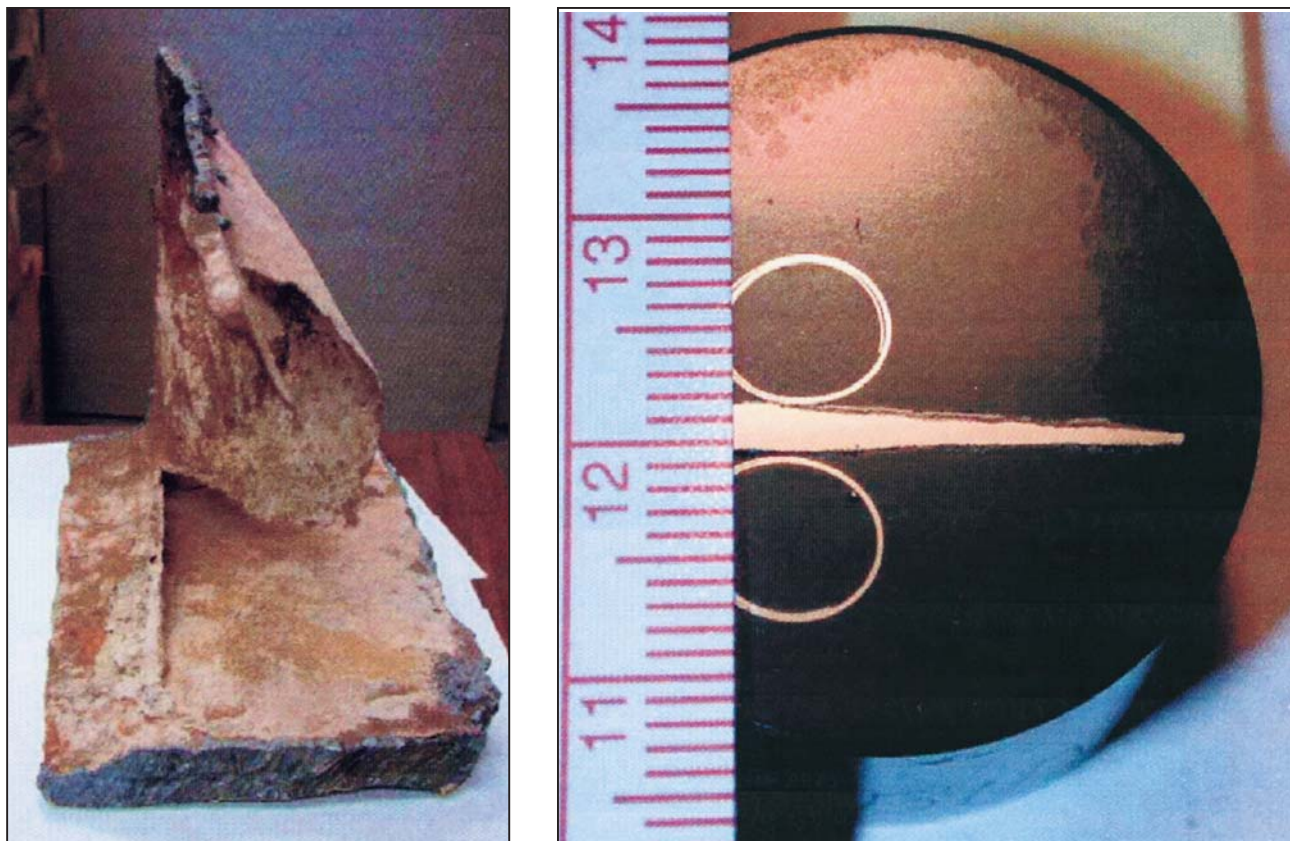


Figure C-9 Qualitative chemical analysis.

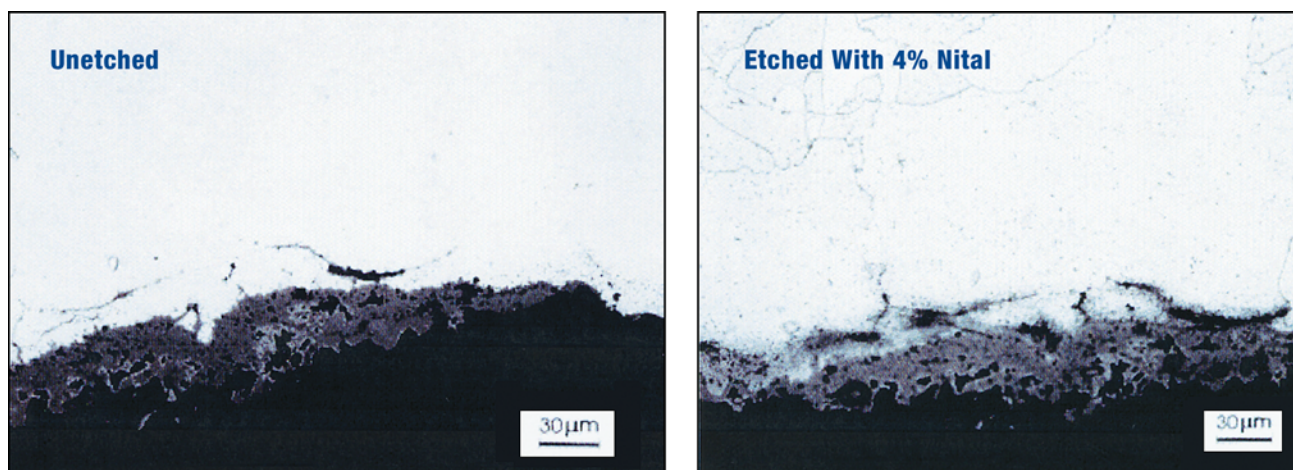


Figure C-10 Grain boundary corrosion attack.

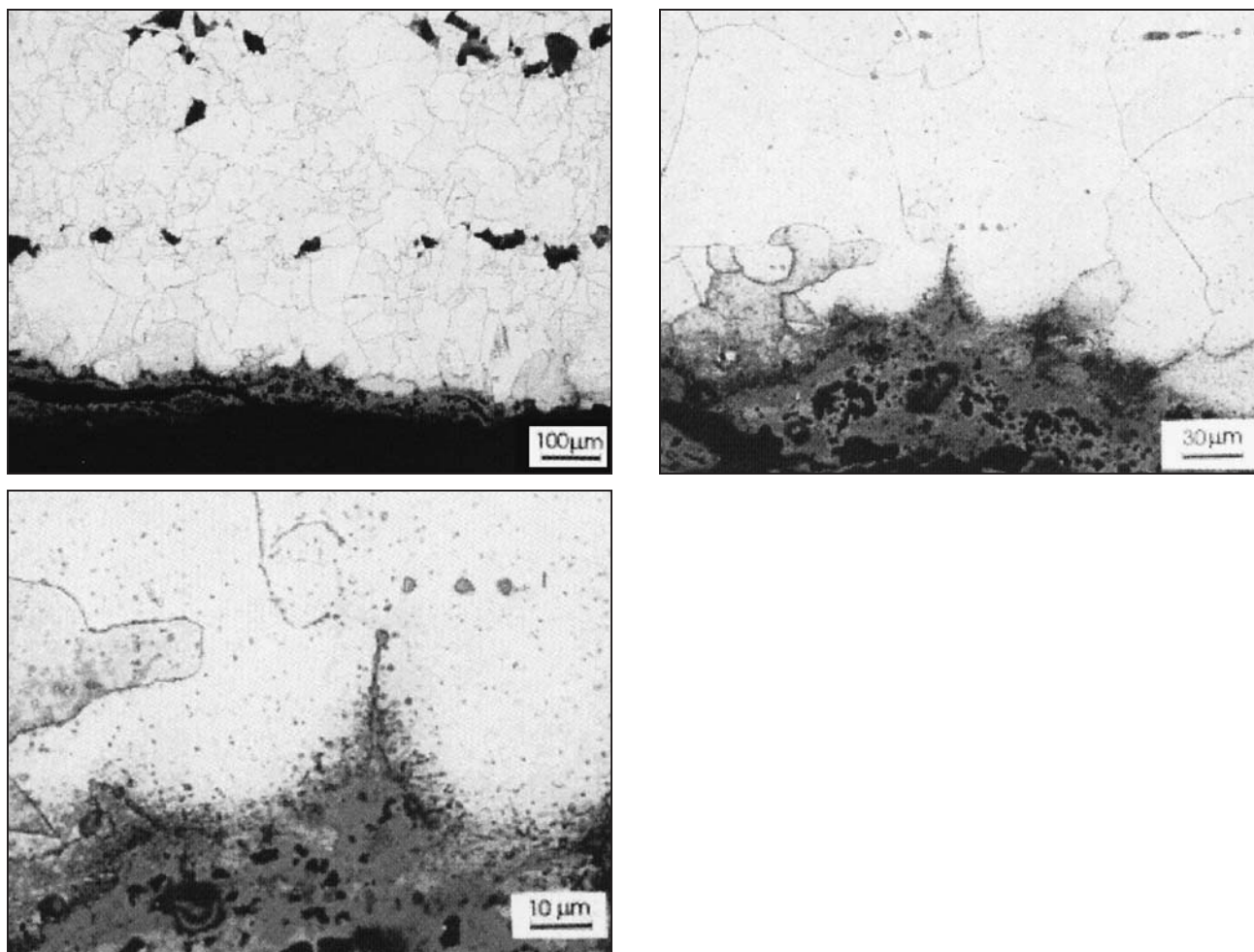


Figure C-11 Microstructure of a typical region showing the surface and grain boundary corrosion attack of Sample 2.

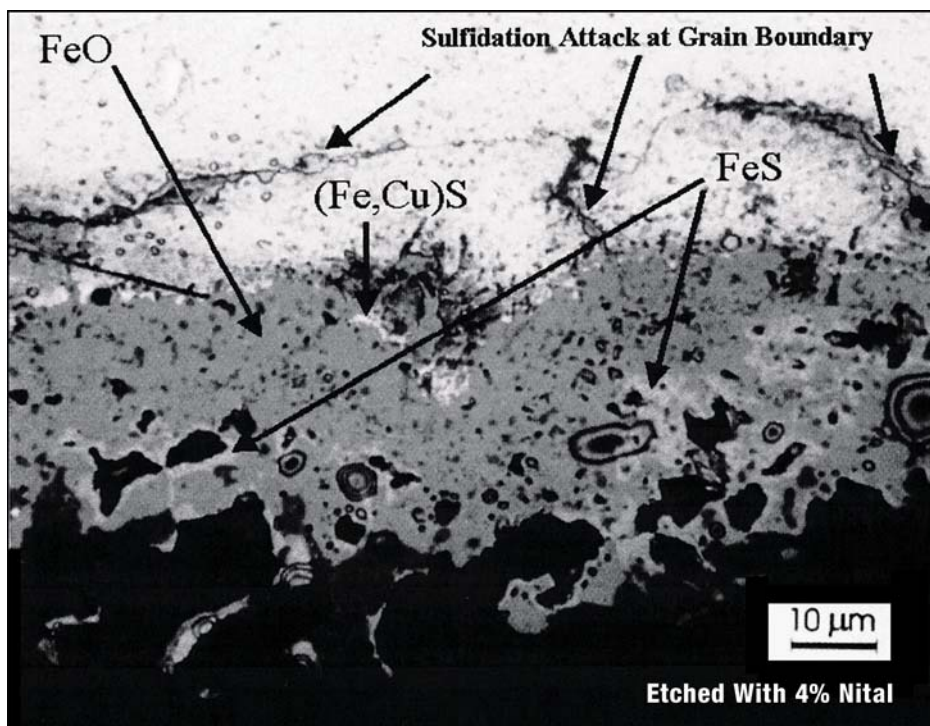


Figure C-12
Higher magnification of the region
shown in Figure C-10.

Figure C-13 shows the region where a qualitative chemical analysis of the eroded region was performed. The comparison of the EDX spectra from the specific regions identified in Figure C-13 shows concentration of copper and sulfur in the grain boundaries in addition to iron sulfide formation adjacent to iron oxide in the oxidized surface layer. Sulfide formation within the steel microstructure increases in concentration as the oxidized region is approached from the steel side. This is clearly shown in Figure C-14.

The larger sulfides further into the steel are the more stable manganese sulfides that were formed when the steel was made. The smaller sulfides that have formed as a result of the fire do not contain significant amounts of manganese, but rather are primarily sulfides containing iron and copper. These sulfides have a lower melting temperature range than manganese sulfide. It is much more difficult to tell if melting has occurred in the grain boundary regions in this steel as was observed in the A36 steel from WTC 7. It is possible and likely, however, that even if grain boundary melting did not occur, substantial penetration by a solid state diffusion mechanism would have occurred as evidenced by the high concentration of sulfides in the grain interiors near the oxide layer. Temperatures in this region of the steel were likely to be in the range of 700–800 °C (1,290–1,470 °F).

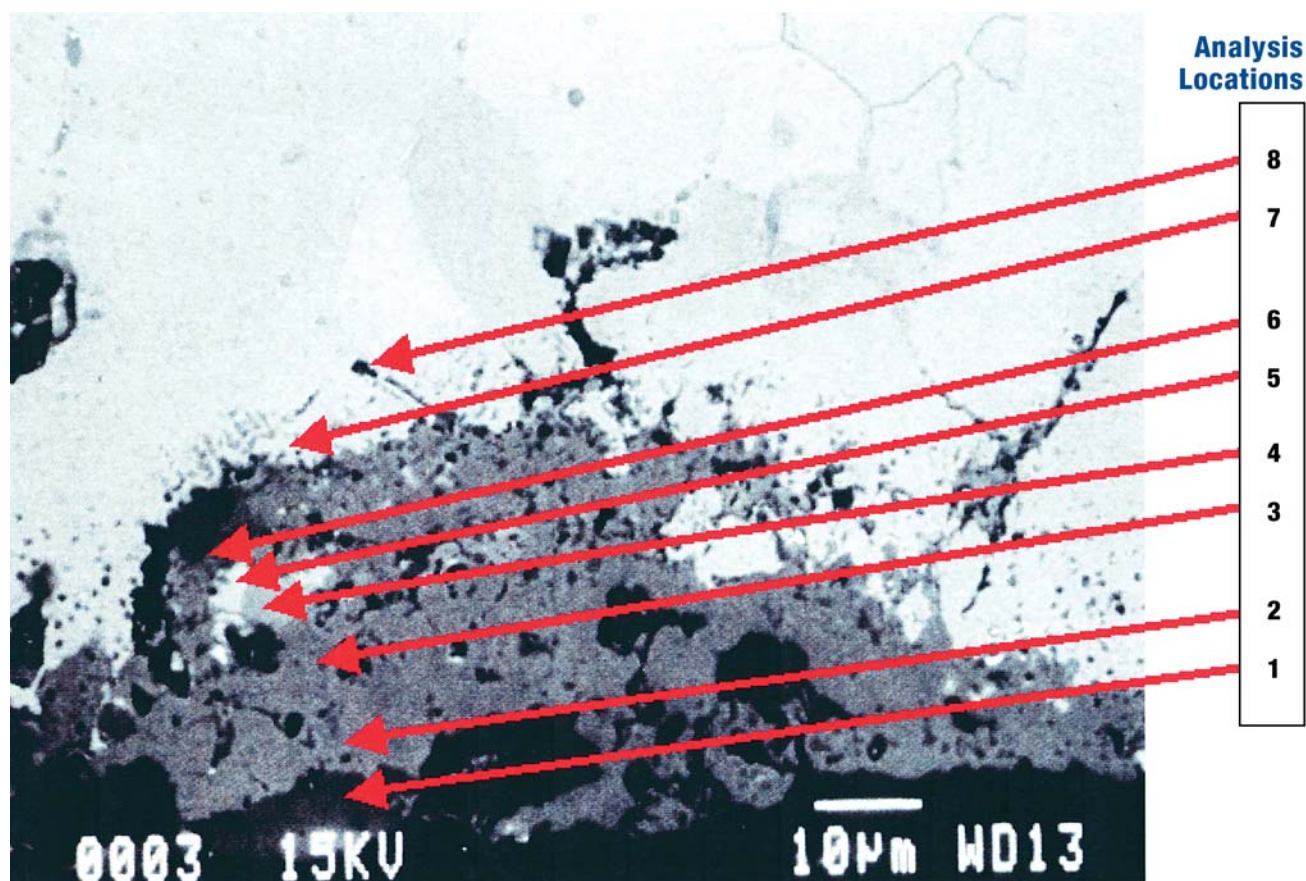
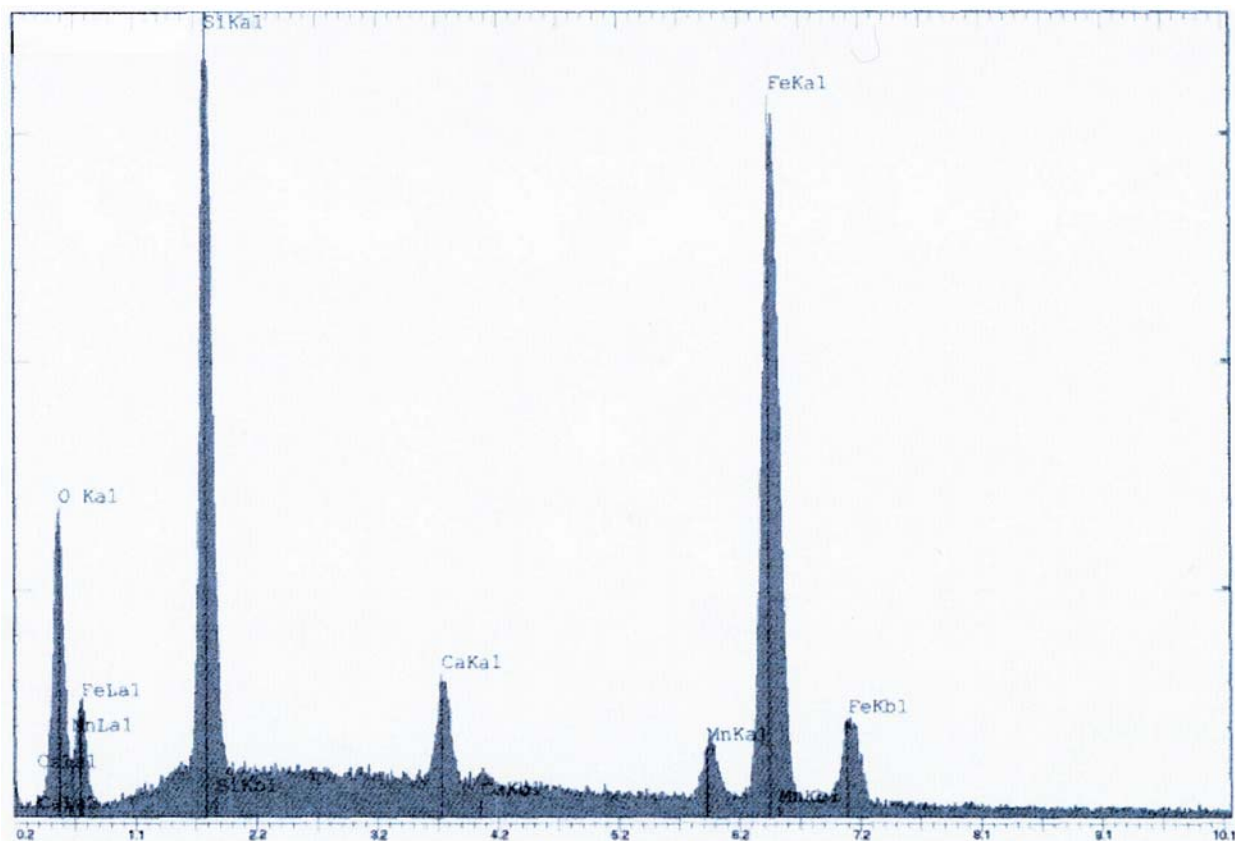
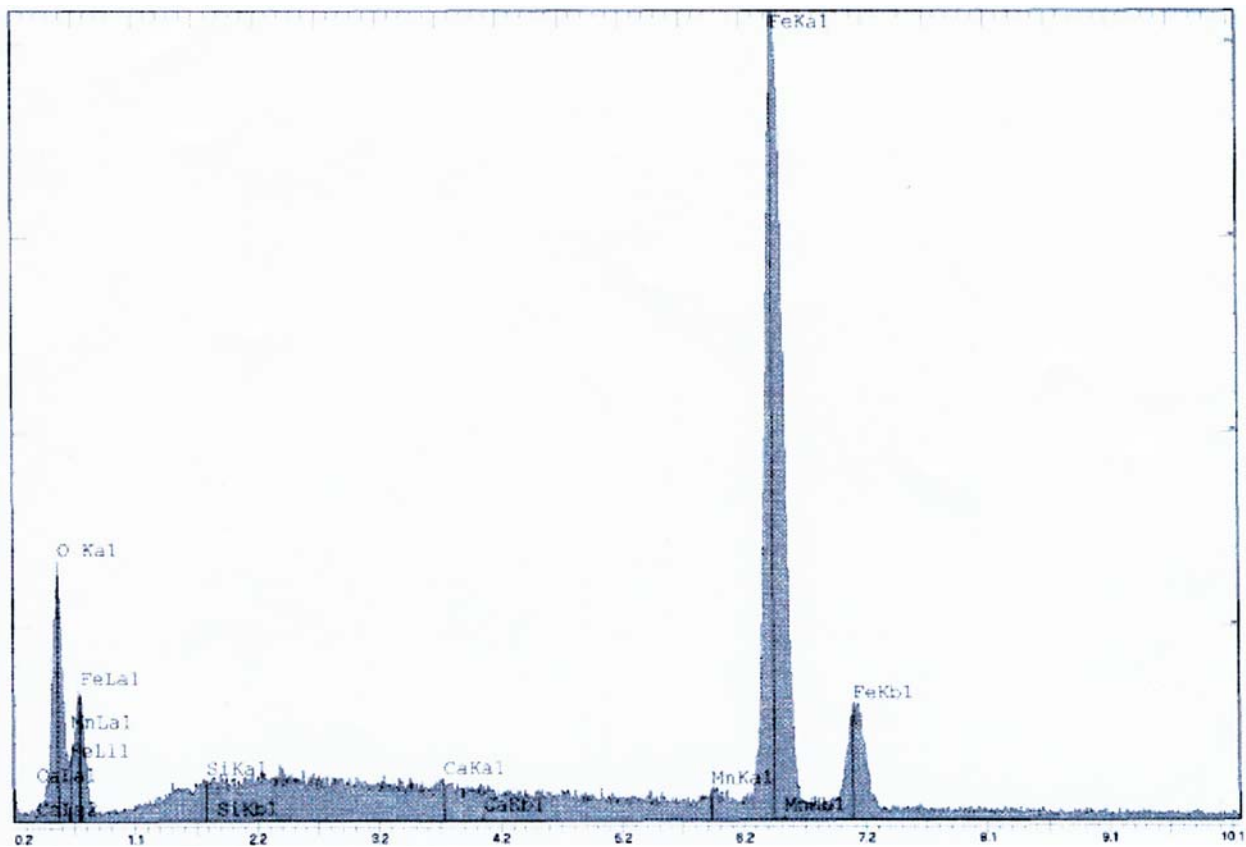


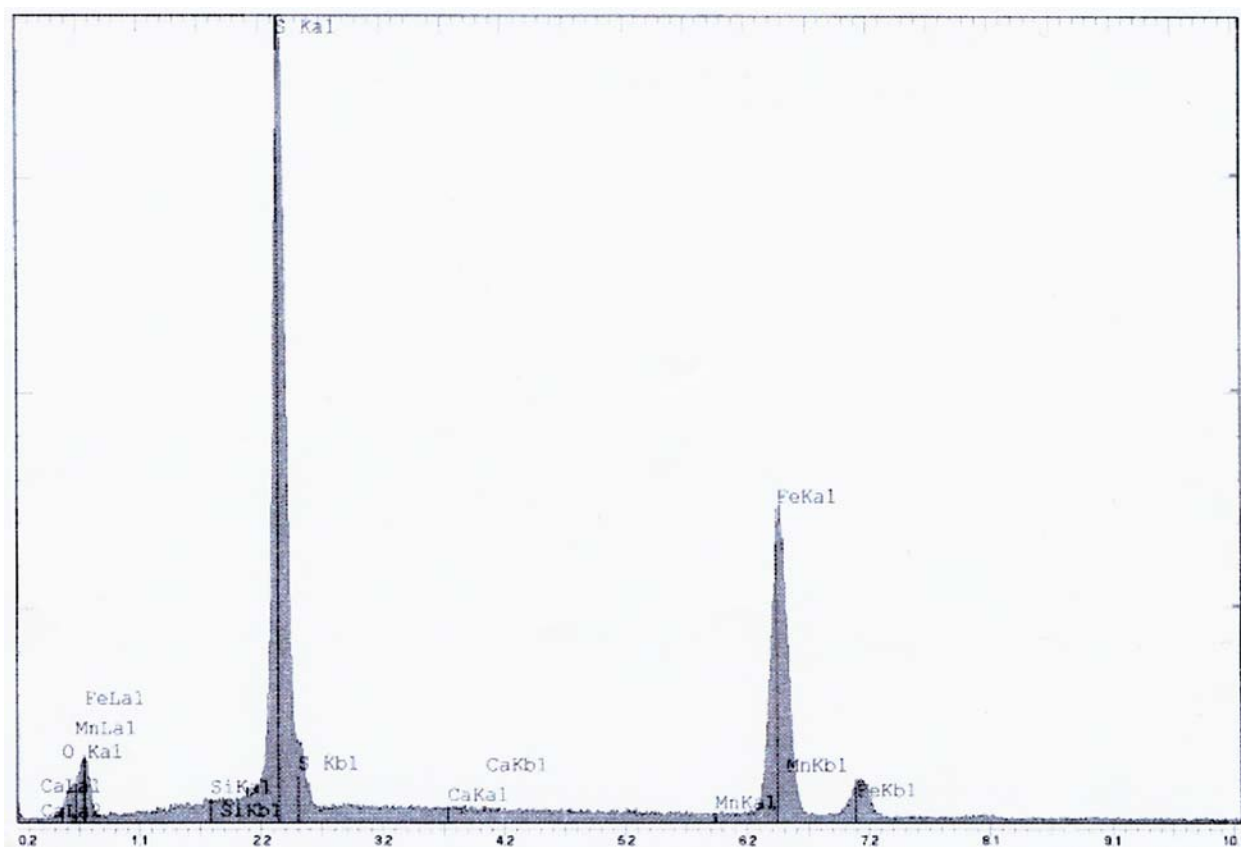
Figure C-13 Regions where chemical analysis was performed.



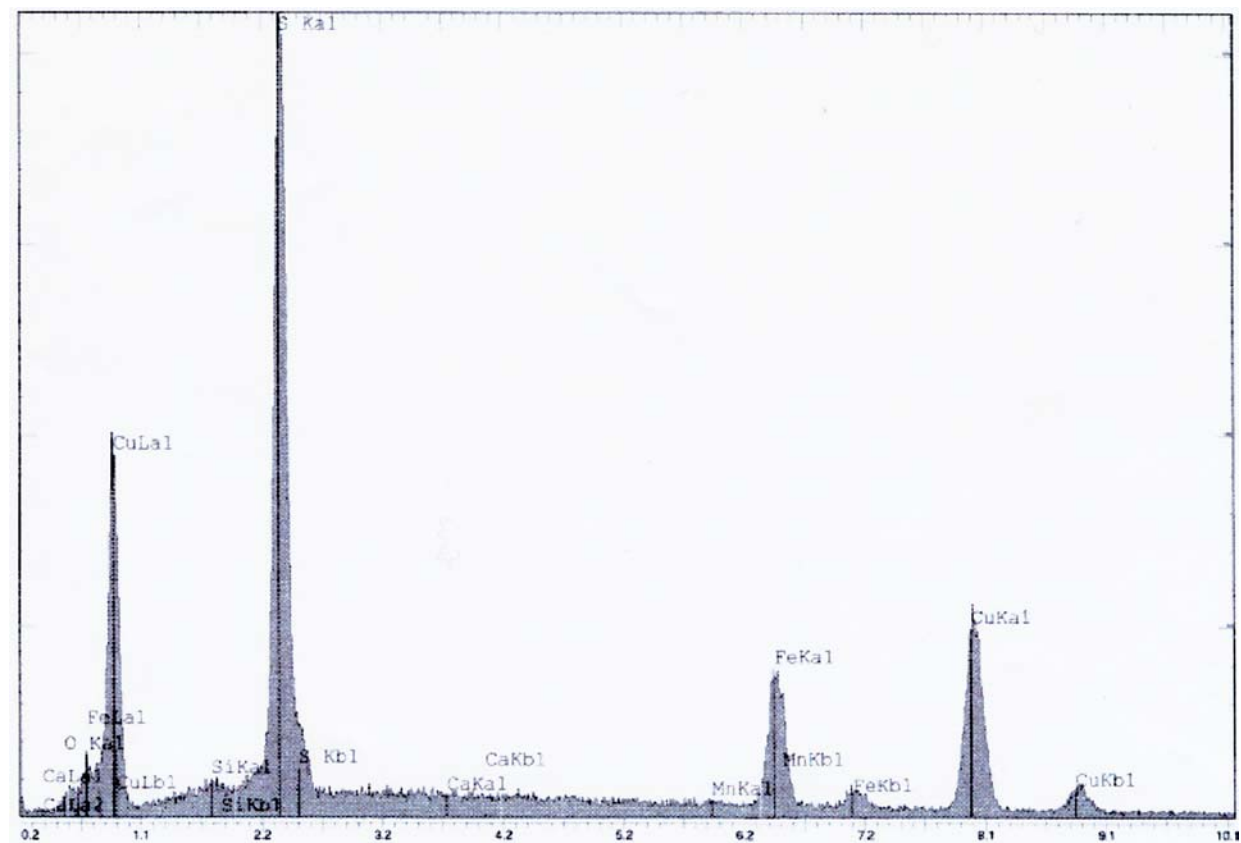
Location 1 (Figure C-13 continued).



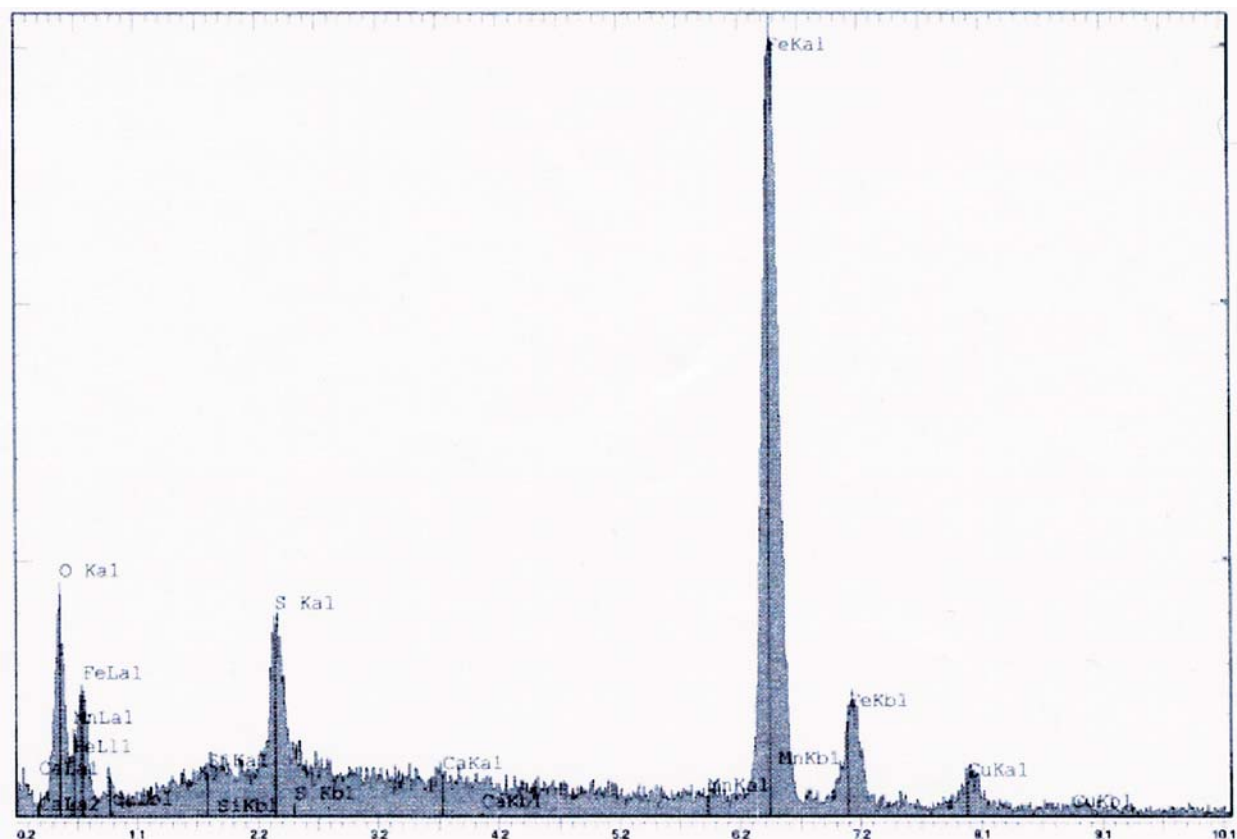
Locations 2 and 3 (Figure C-13 continued).



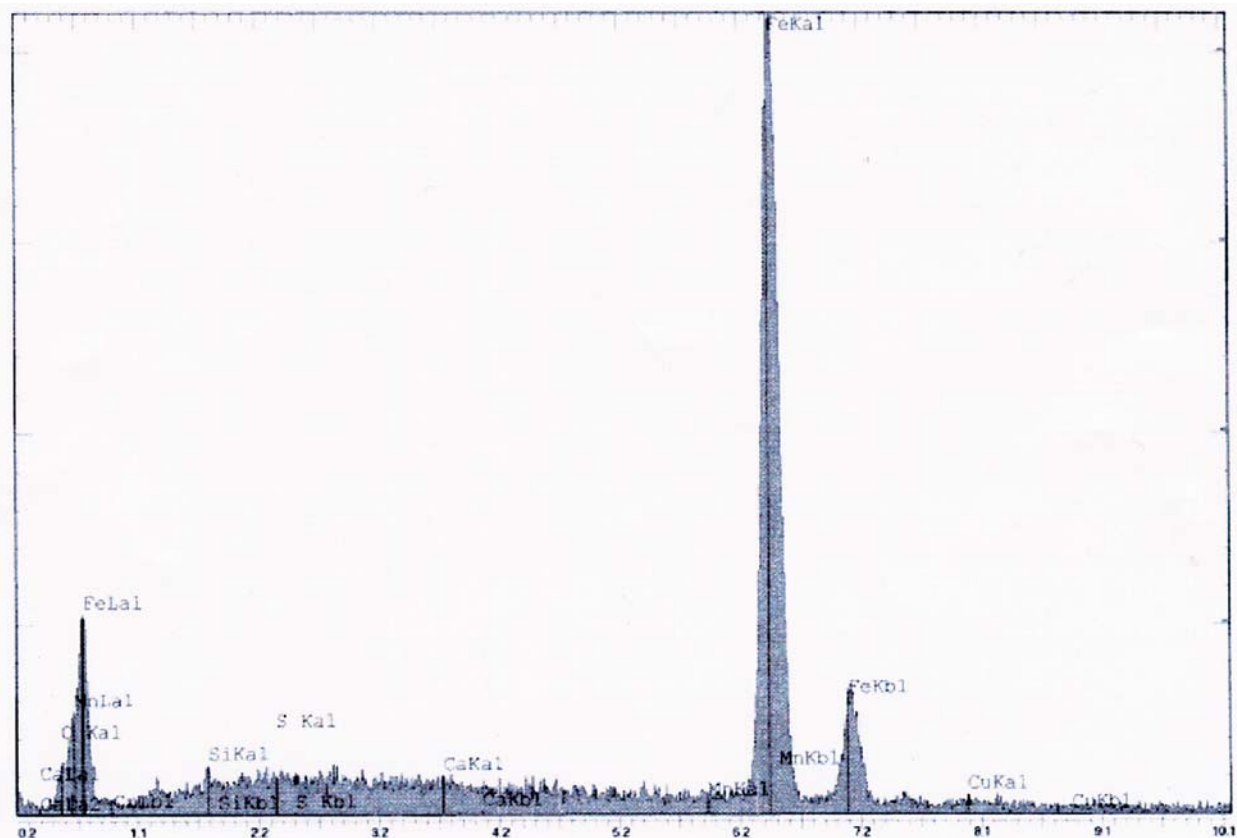
Location 4 (Figure C-13 continued).



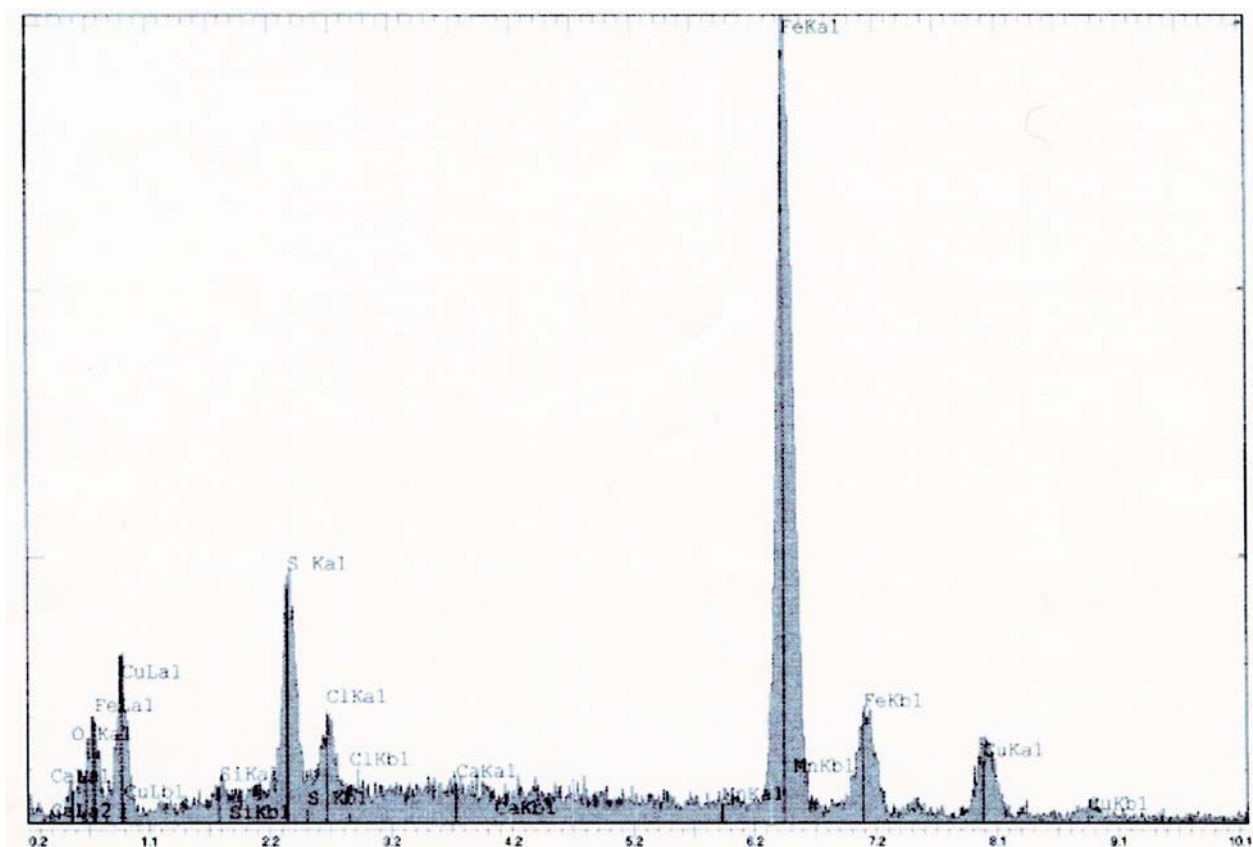
Location 5 (Figure C-13 continued).



Location 6 (Figure C-13 continued).



Location 7 (Figure C-13 continued).



Location 8 (Figure C-13 continued).

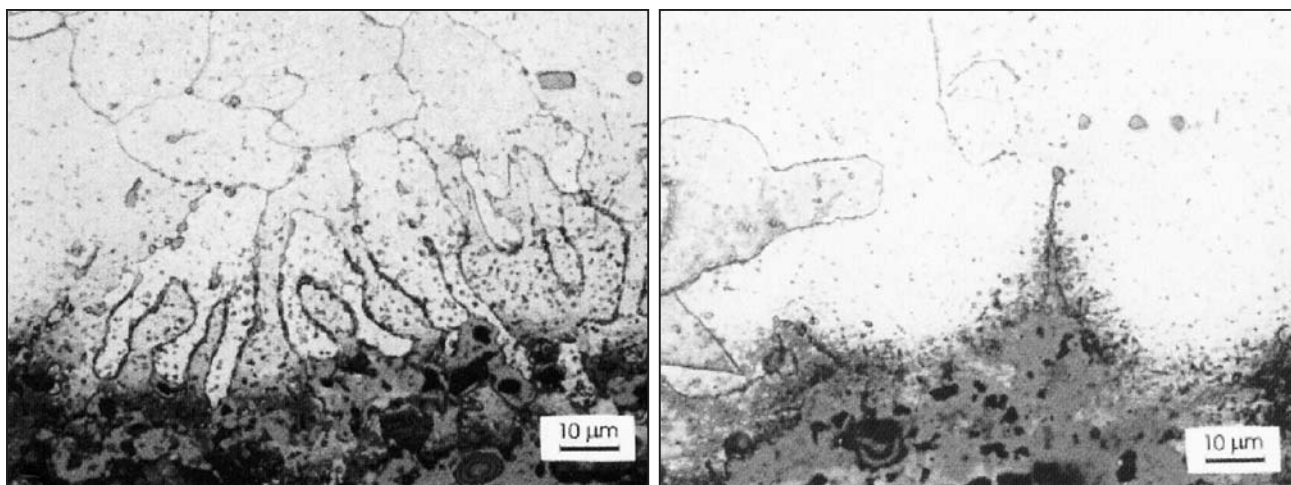


Figure C-14 Gradient of sulfides into the steel from the oxide-metal interface.

C.5 Summary for Sample 2

1. The thinning of the steel occurred by high temperature corrosion due to a combination of oxidation and sulfidation.
2. The sulfidation attack of steel grain boundaries accelerated the corrosion and erosion of the steel.
3. The high concentration of sulfides in the grain boundaries of the corroded regions of the steel occurred due to copper diffusing from the HSLA steel combining with iron and sulfur, making both discrete and continuous sulfides in the steel grain boundaries.

C.6 Suggestions for Future Research

The severe corrosion and subsequent erosion of Samples 1 and 2 are a very unusual event. No clear explanation for the source of the sulfur has been identified. The rate of corrosion is also unknown. It is possible that this is the result of long-term heating in the ground following the collapse of the buildings. It is also possible that the phenomenon started prior to collapse and accelerated the weakening of the steel structure. A detailed study into the mechanisms of this phenomenon is needed to determine what risk, if any, is presented to existing steel structures exposed to severe and long-burning fires.