Metallographic Examination of Heavily Eroded Structural Steel from World Trade Center Buildings 1, 2 and 7

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Steel samples from Buildings 1, 2 and 7 of the World Trade Center were collected during the Federal Emergency Management Agency forensic investigation shortly after the September 11, 2001 incident. Macroscopically, the steel samples supplied exhibited severe "erosion" with plate thickness varying from 12.7mm to a total loss of metal in many areas. Also, some localized plastic deformation was observed. A determination of the cause of this unexpected erosion and an estimate of the maximum temperature that this steel likely experienced are the subjects of this paper.

INTRODUCTION

The collapse of World Trade Center Building 7 (WTC 7) is of significant engineering interest because it appears that its collapse was due primarily to fire, rather than any impact damage from the collapsing WTC 1 tower [1]. The Federal Emergency management Agency (FEMA) investigation team noted that there was little, if any, record of fire-induced collapse of large fire-protected steel buildings prior to this event. In their analysis, the WTC 7 building collapse was consistent with an initial failure that occurred internally in the lower floors toward the eastside of the building. Fire ignition is thought to have started as a result of falling debris from WTC 1 damaging the south face of WTC 7. The fire progressed throughout the day, unimpeded by manual or automatic fire suppression systems. The fire got hotter as time progressed and the building collapsed about 7 hours after the collapse of WTC 1. The FEMA team further noted that although the total diesel fuel on the premises contained massive potential energy, this likely energy source had only a low probability of occurrence. Their conclusion was based on the fact that there was no physical, photographic or any other evidence to either substantiate or

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refute the discharge of fuel oil from the piping system. Can a microstructural examination of the steel give insight into why WTC 7 collapsed?

MATERIALS AND EXPERIMENTAL PROCEDURE

The FEMA team obtained the structural steel examined in this study. The steel from WTC 7 was ASTM A36. The nominal composition of A36 is 0.28% C max, 0.8-1.2% Mn, 0.04% P, 0.05% S, 0.15-0.3% Si balance Fe. The asfabricated wide flange beam analyzed had a microstructure that consisted of a banded hot worked mixture of ferrite and pearlite as shown in Fig. 1. The structural steel column that was examined was from either WTC 1 or 2 and was known to be a high strength structural steel, and not A36. Since chemistry control for structural steels is generally quite liberal, the exact ASTM designation was not known. The nominal composition of this steel is 0.15% C max, 1.00% Mn max, 0.04% P max, 0.04% S max, 0.2% Cu min with a possible Si addition and residual amounts of gases, such as N and O, and elements (small amounts of these could be deliberate additions, depending upon the grade and steelmaker) such as Cr, Mo, Ti, V, Nb and Zr (with the balance being Fe) similar to an ASTM A242 grade high-strength, low-alloy (HSLA) steel. The as-fabricated column microstructure consisted of a banded hot worked mixture of ferrite and pearlite as shown in Fig. 2. The grain size is somewhat coarser and there is substantially less pearlite than observed in the A36 steel. Also, a fine dispersed phase is observed in the ferrite regions at higher magnification. Severe erosion reduced the cross sections in both steels from a nominal 12.7-mm to less than a millimeter as shown in Fig. 3.





FIGURE 1 (left) Ferrite-pearlite microstructure of an unaffected A36 beam area (nital etch).

FIGURE 2 (right) Ferrite-pearlite structure of an unaffected HSLA column area (picral etch).



FIGURE 3 Examples of the severe loss of section thickness in the A36 beam (left) and HSLA column sections.

Microstructural analysis investigations were conducted using standard light optical microscopy and scanning electron microscopy with energy-dispersive analysis techniques. Specifics will be noted when appropriate.

OBSERVATIONS AND DISCUSSION

WTC 7

In severely "eroded" areas in the A36 steel, where the thickness had been reduced substantially, heating in a hot-corrosive environment was evident in the microstructure. Chemical reactions including oxidation, sulfidation, and decarburization occurred as well as all of the usually observed equilibrium phase transformations in the steel. An example of a typical near-surface microstructure is shown in Fig. 4. This microstructure shows the scale and slag reaction effects at the top of the photomicrograph and the normal metallurgical reactions that occurred in this steel on heating and cooling toward the bottom. As the temperature increased changes in the microstructure of the steel occurred simply as a result of heating and cooling. However, as higher temperatures occurred, microstructural, as well as chemistry changes, resulted. The interaction of heat in a corrosive fire environment resulted in making this steel susceptible to sulfidation and severe erosion.

As the temperature increases, several reactions normally occur within the steel. Two important intermediate temperature transformation reactions occur to soften the steel. These are the pearlite spheroidization reaction and the conversion from ferrite to austenite on heating followed by transformation back to pearlite and ferrite on cooling. Typical examples of these transformations are presented in Fig. 5 and Fig. 6 from pearlite banded regions near the bottom of Fig. 4. In Fig. 5 the Fe₃C in the pearlite had started to spheroidize. Also, some pearlite bands have areas where a re-austenitization had occurred and new finer grained regions of pearlite and ferrite formed on cooling as shown in Fig. 6. These observations suggest that the steel in this region had experienced temperatures in the range of 550 to 850 °C.



FIGURE 4 Near-surface transformations in the A36 beam: intergranular penetration of the liquid eutectic of FeO and FeS, subsurface decarburization and dissolution of the pearlite (nital etch).



FIGURE 5 (left) SEM view of the start of spheroidization of lamellar cementite in the A36 steel beam (nital etch).

FIGURE 6 (right) Recrystallization of ferrite in areas where the pearlite has been partially dissolved (nital etch).



FIGURE 7 Color micrograph showing the growth of columnar ferrite grains beneath the oxidized surface (nital/Beraha's reagent).

At higher temperatures, in the ferrite + austenite phase field region, the chemical reaction rate of carbon loss to the atmosphere increases in addition to the phase transformations. Substantial decarburization can occur in this two-phase region and result in a columnar ferrite grain morphology under the scale on the steel. An example of this microstructure is shown in Fig. 7. Columnar geometry ferrite grains form in this steel as a result of loss of carbon and grain growth under a fixed compositional equilibrium requirement. This transformation likely occurred in the range of 750 to 900 °C. Toward the right side of Fig. 7 a liquid penetration into the steel had occurred when the steel was hot and transformed on cooling to the eutectic mixture of iron oxide and iron sulfide [2]. If these phases are pure FeO and pure FeS, the eutectic temperature is 940 °C [3]. However, incorporation of other elements into the liquid would likely lower the eutectic temperature.

At 940 °C and higher, iron, sulfur and oxygen form a liquid (possibly a sulfate) that penetrates into the iron oxide grain boundaries forming a mixture which dissolves the iron oxide forming a semi-solid with the liquid at the eutectic composition. The semi-solid region is composed of nearly spherical solid iron oxide particles dissolving into the sulfur rich liquid. This is shown in Fig. 8.

The transformed microstructure from the section of the steel beam shown in Fig. 8 shows that the steel had reached a temperature at which it was fully austenitic and had undergone substantial grain growth. The severe erosion observed is a result of sulfidation caused by liquid penetration into the austenite grain boundaries resulting in large grain pullout of material due to a liquid intergranular attack. This liquid transforms isothermally to a two-phase eutectic product on cool-down. Digital x-ray maps for the distribution of iron, oxygen and sulfur in the eutectic reaction region are shown in Fig. 9. Sulfidation in the solid state into the austenite grains occurs much slower and is observed on cooling as a gradient of precipitated sulfides and oxides or oxidized sulfides with many of these particles containing silicon. The oxide scale in Fig. 8 is a multi-phase mixture that occurred on cooling. It can contain different mixtures of retained wustite (FeO), magnetite (Fe₃O₄) and some hematite (Fe₂O₃) depending on cooling rate effects. The amount of liquid and solid formed in the semi-solid region as well as the multi-phase oxide mixture observed suggests a maximum steel temperature near 950 °C.



FIGURE 8 Example of the oxide-sulfide scale and grain-boundary penetration (nital etch).



FIGURE 9 SEM image and x-ray elemental maps for S, Fe, O and Si.



FIGURE 10 Example of the attacked surface of the HSLA column (not etched) showing copper at the steel-scale interface and in the grain boundaries with substantial sub-surface oxide/sulfide precipitation.

WTC 1 or 2

The microstructure of a severely eroded column section from either WTC 1 or 2 was examined using a similar approach to that used to characterize the A36 steel beam from WTC 7. The microstructure of this HSLA steel revealed corrosion reactions similar to those observed in the WTC 7 steel. However, there were substantial differences due to the lower carbon content and the copper alloy additions. A typical microstructure of the near surface damage is presented in Fig. 10. High temperature sulfidation and oxidation occurred with substantial grain boundary sulfidation under a well-bonded scale. The scale that formed on the steel was nearly continuous and contained a mixture of iron oxide, iron sulfide, and copper sulfide. The morphology of this mixture, while significantly different from that observed on the A36 steel, experienced a similar hot-corrosive attack. A gradient in sulfur penetration of the oxide scale from the atmosphere inward was observed along with the dissolution of the iron oxide into a semisolid mixture.

A digital x-ray map of the distribution of major elements through the scale and into the steel is shown in Fig. 11. Sulfur penetration into the oxide scale reacts to form iron sulfide and copper sulfide and a fluxing reaction occurs resulting in sulfur penetration into the steel forming predominantly manganese sulfides in many of the prior ferritic grain boundaries on cooling. It is much more difficult to detect liquid formation in these boundaries prior to cooling and the additions of copper and silicon complicate the formation of a simple eutectic product. However, the etching response at the grain boundaries of the steel and the formation of a columnar-grained geometry, suggests a thin film liquid corrosive penetration into the boundaries as shown in Fig. 12. More research is necessary to clarify the sulfidation reactions that occur in this HSLA steel.



FIGURE 11 SEM image and x-ray elemental scans for Fe, Cu, S, O and Si at the affected surface of the HSLA column.



FIGURE 12 Example of grain-boundary decoration by the eutectic attack in the HSLA column material (nital etch).

PRELIMINARY LABORATORY SIMULATION RESULTS

The results of a laboratory heating experiment at 1100 °C for 12 hours where an iron sulfide (FeS) powder was placed on ground and cleaned A36 steel surface prior to heating is presented in Fig.13. The microstructure that developed showed oxidation, sulfidation and eutectic liquid reactions that are quite similar to the microstructure that formed on the WTC 7 steel in the fire. This similarity suggests that when an iron sulfide phase forms on or with the oxide, intergranular attack by a liquid containing Fe, S, and O will occur if the temperature is sufficiently high.

Internal sulfidation and oxidation is also observed in Fig.13. The "dark spots" in the microstructure were found by EDS analysis to contain Mn and S, as well as Si and O. The inward concentration gradient of particles beneath the steel surface indicates a diffusion controlled internal reaction is occurring in this steel. Again, this is similar to the reactions observed in the WTC 7 steel beam. A thermodynamic analysis of the Fe-S-O system with additions of Mn, Si, and Cu is currently underway to determine the conditions that would form these sulfidation and oxidation products.



FIGURE 13 Example of eutectic attack and internal oxidation/sulfidation in the HSLA column material at the surface.

CONCLUSIONS

WTC 7

Rapid deterioration of the A 36 steel was a result of a hot corrosive attack involving decarburization, oxidation, and sulfidation. Heating A 36 steel in an environment containing oxygen and sulfur resulted in intergranular melting which transformed to an iron oxide-iron sulfide eutectic mixture on cooling.

The reaction forming the eutectic lowers the temperature at which liquid can form in this steel to about 940 °C, or possibly lower, depending on the amount of silicon, carbon, and other impurities dissolved into the liquid eutectic. Isothermal furnace experiments at 1100 °C using iron sulfide powder placed on ground A36 steel produced a hot corrosive reaction with liquid penetration similar to that found in the steel in the WTC 7 fire.

WTC 1or 2

Severe thinning of the HSLA steel occurred by high temperature corrosion due to a combination of oxidation and sulfidation. Sulfidation of the grain boundaries in the HSLA steel accelerated the degradation of the steel. The high concentration of sulfides in the grain boundaries in the corroded regions of the steel involved copper diffusing from the alloy combining with iron, manganese, silicon and sulfur forming both discrete and continuous sulfides in the grain boundaries of the steel suggesting the presence of a liquid phase.

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