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A Study on the Corrosion and Degradation of Boiler Tubes Steel in Fossil Power Plant

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It was analyzed the causes of boiler tube rupture due to a degradation and corrosion on the boiler tubes in fossil power plant. The experiments were carried out among samples taken from the operating facilities. The result were analyzed based on experimental results from mechanical strength, microstructure observation, and hardness measurement in order to determine the cause of local rupture on boiler tubes. In general, 2.25Cr-1Mo steel generates carbides, it is coarsened, its ductility and strength abruptly decreased as degradation is in progress, In order to confirm this phenomenon, we observed changes of the mount of Cr and Mo of carbide by carrying out EDX chemical composition analysis. The amount of Cr and Mo in the degraded material or service exposed material gradually increased the amount of Mo but initially they were almost maintained at the same amount. Furthermore, we observed that the carbide become coarsened both in the grain and at the grain boundary. Tensile test was carried out to measure a material hardness and to recognize a drop-off of hardness. Overall result for tensile strength and hardness turned out to be lower than new material and mechanical strength and hardness was degraded as the material degradation was in progress.

Keywords : *fossil power plant, reliability evaluation, 2.25Cr-1Mo steel, material degradation, tensile test, carbide, hardness test, nondestructive test, toughness*

1. Introduction

In case of the materials in elevated temperature environment for a long time, the material aging degradation occurs, which decreases mechanical properties and fracture toughness of the materials due to decrease the amount of solid solution reinforcement elements in matrix region, generation and coarsening of the carbide, recovery of dislocation structure, etc. These drawbacks curtail the facility life. In the worst case, it may cause the facility equipment to fracture unpredictably, eventually lead to suffer from economical loss. Therefore, it is needed to develop a degradation evaluation method in the perspectives of reliability of structure. In general, it is accurate results to evaluate material aging degradation via destructive methods such as impact test, tensile test and fracture toughness test relatively would be an accurate evaluation methods but in the ongoing facility it would encounter many challenges not to damage the facility and to sample the specimen. Accordingly, nondestructive test to be capable of evaluating material degradation of the structure has been researched in these days. Because the facilities degradation in elevated temperature depends on many factors from microscopic changes to macroscopic changes. thus it can be evaluated by the different evaluation method based on its using conditions and environments. Recently, microstructure observation, hardness test, grain boundary corrosion test, electrical resistivity measurement, electro-magnetic method, and acoustic emission have been widely used as a nondestructive methods for damage evaluation of the fossil power plan.[2)-4)]

In this study, using destructive method, the possible causes of the tube rupture analyzed via measuring the mechanical strength, hardness and microstructural degradation of the boiler reheater tube and superheater tube steel.

2. Experimental methods

2.1 Experiment material and specimen manufacture

The material used in this study is 2.25Cr-1Mo Steel (JIS STBA 24), which is widely used as a material of reheater tube in fossil power plant, composed of C; 0.12, Si; 0.38, Mn; 0.46, P; 0.063, S; 0.0087, Ni; 0.055 (wt%). In order to make specimens needed for inspection of the facility degradation, samples were taken from the service

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exposed tubes used for 151,000 hours. Specimens were prepared to perform tensile test, microstructural inspection, and hardness test.

2.2 Degradation evaluation test

In order to evaluate the degree of the material degradation, the microstructure and carbide of specimen taken from a ruptured tube were observed with an optical microscopic and SEM to measure its metallic changes. In particular, EDX chemical composition analysis performed to know the distribution of Cr and Mo on carbide, which are the main components of carbide distributed in the grain and grain boundary. The tensile test was performed to inspect changes of the mechanical characteristics of the service exposed material under room temperature. Tensile test was carried out using 10 tone force hydraulic tester (SHIMADZU). Test velocity was 0.01 mm/sec. In addition, hardness changes of material was measured by using Viker's hardness tester to know the hardness changes of service exposed material,

3. Experimental results and analysis

3.1 Inspection corrosion status

The cross section of the ruptured areas in reheater tube was presented in Fig. 1. As shown in Fig. 1, a mount of scale are inspected caused by corrosion in inner and outer parts of the tube. The chemical composition analysis was performed to analyze the major components of corroded areas. it turned out to be Hematite(Fe_2O_3), which is a kind of oxide irons.

Table 1. Chemical composition analysis upon the corrosion layer

Fe_2O_3	SiO_3	CaO	MgO	Al_2O_3	NiO	ZnO	Cr_2O_3	MnO
89.14	1.19	1.76	0.13	0.4	0.34	0.36	2.19	0.38

When you look at the progress of corrosion as shown in Fig. 1(b), inner parts of fresh part become oxidized continuously and its outer parts of corrosion layer become detached because of collision between flowing particles inside of boiler. Thus, the oxidization gets iterated, resulted from decrease of outer diameter Compared to the outer parts of the tube, the corrosion layers keeps growing rather than being excluded.

The scales was excluded from the deformation region of the tube when the shape of tube is locally deformed as shown in Fig. 1.

The corrosive attack make the diameter of fresh region thinner to the certain degree, the tubes get elongated, being

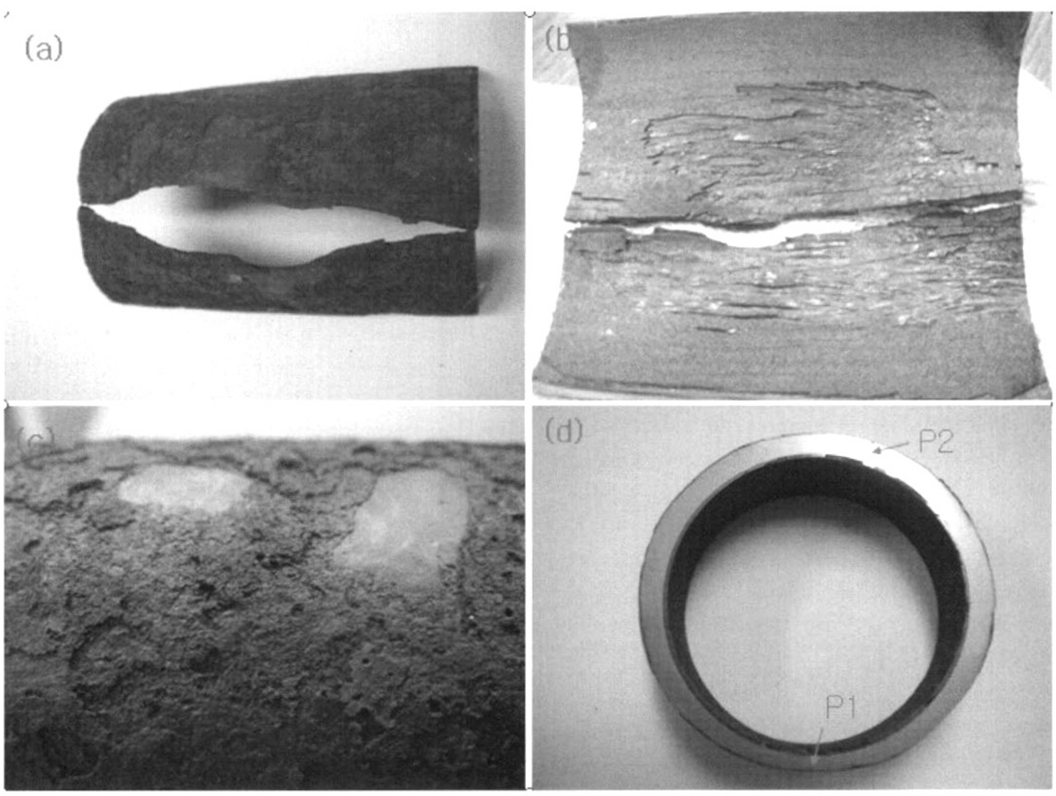

Fig. 1. Rupture status of reheater tube.

affected by creep deformation and finally, they are ruptured. In this process it is considered that the inner parts of corrosion layers would be excluded during creep deformation. In case of the ruptured tube, it was observed that the thickness of fresh part not being corroded becomes decreased and the diameter of the tube gets elongated asymmetrically by creep deformation.

3.2 Microstructural observation and chemical composition analysis

Optical microscope pictures on the specimen was taken, which sampled from ruptured area (Fig. 1(d)) and the opposite side of the rupture(Fig. 1(d)). As shown in Fig. 2, it were identified that the degradation of microstructure was quite a large progress due to the long period of ex-

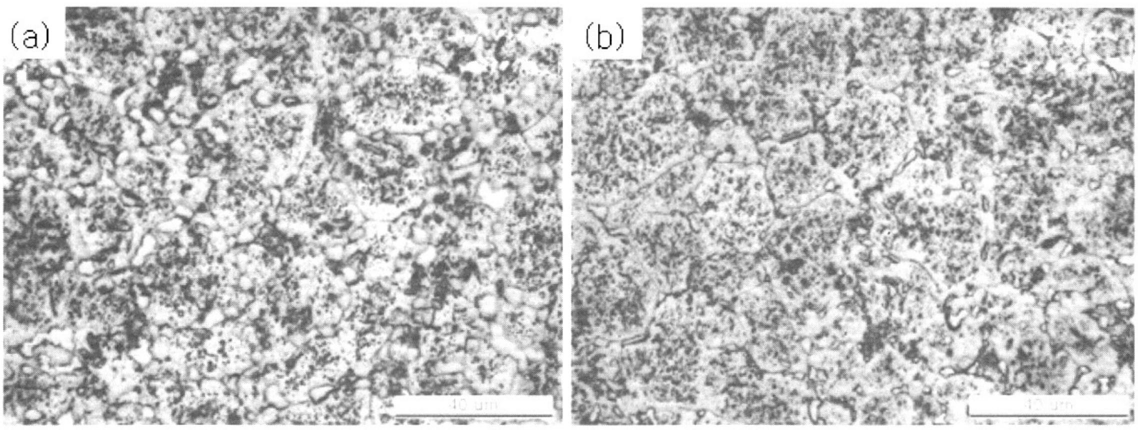

Fig. 2. Optical microscopic observation on the ruptured reheater tube
(a) optical microscope on the thickness reduction part.
(b) optical microscope on the opposite part of thickness reduction part

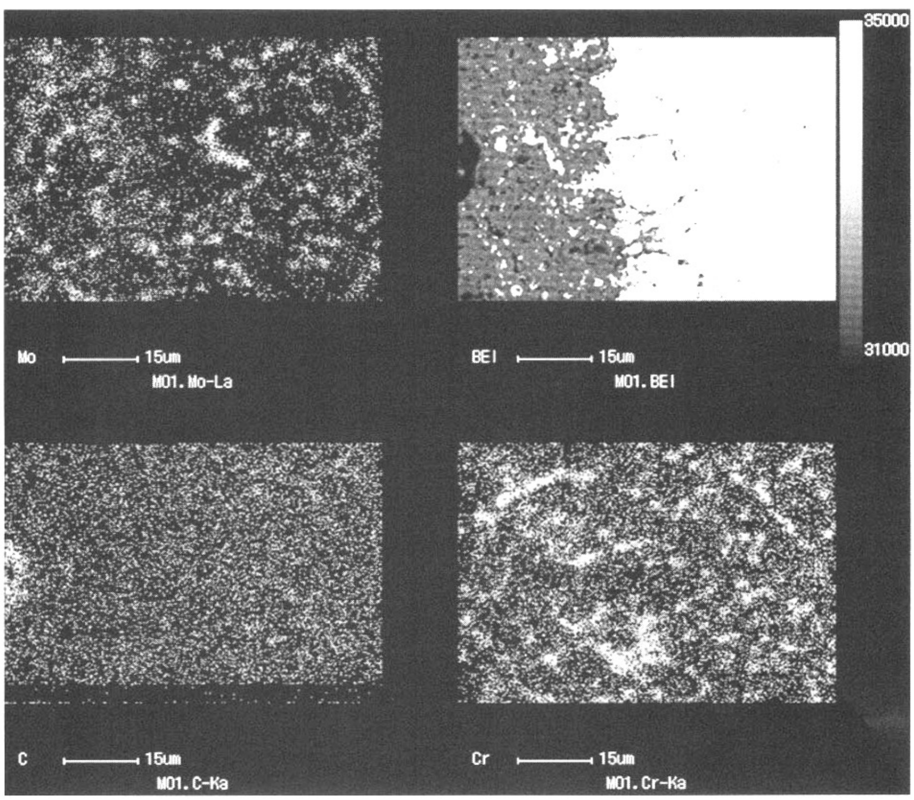

Fig. 3. Cross section microstructure and EDX analysis on the corroded region in reheater.

posure in elevated temperature. In the thickness reduction part as shown in Fig. 2(a), Cr and Mo carbide assumed get coarsened along the grain and grain boundary. It is considered that the aging degradation, which it is well known degradation phenomenon in this material, has been considerably developed in the large area.

SEM and EDX analysis were carried out with the specimen sampled from the rupture are (Fig. 1(d)) and the opposite side of the rupture area (Fig. 1(d)). The cross section area of the boundary region between the corrosion layer and the fresh region was shown in Fig. 3. It can be identified that the corrosion fraction is locally in progress and the density at the cross section is distributed inhomogeneously and the different shapes of the pores are distributed irregularly as well. As mentioned in Fig. 2, Cr and Mo are distributed along the grain boundary intensively, formating the bend shape. In case of carbide, it is relatively evenly distributed. The reduction parts in the ruptured tube are also examined by SEM and EDX analysis. As shown in Fig. 4, pearlite vanishes and many carbide extracted from grain boundary and in grain are largely distributed in this microstructure.

Table 2. EDX analysis in grain and grain boundaries on rupture area

composition / position	Cr (wt%)	Mo (wt%)
A	9.29	9.73
B	1.06	0.65

Table 2 shows the result of EDX analysis in grain and the grain boundary on rupture area. In the beginning stage of the degradation, the amount of Cr and Mo in the grain does not differ from the amount of new material(Cr; 2.25wt%, Mo; 1wt%) relatively but as time goes on, Cr and Mo used to solid solution reinforcement elements are precipitated with the shape of the carbide in grain and on the grain boundary. Eventually, material strength abruptly is decreased. Fig. 5 shows the weight composition ratio of Cr and Mo with the degree of degradation (Larson-Miller Paramete; LMP) through EDX analysis above material.[6] Here, LMP is defined as LMP=T(20+logt), T as absolute temperature, t as operating time. In general, LMP is defined as the degree of the degradation of particular material and higher its value increases, the more he degradation progresses. In the Figure, y axis indicates the component ratio of service exposed materials, the weight percent of Cr and Mo in carbide divided by that of Cr(2.25 wt.%) Mo(1.0 wt.%) of new material, respectively. In the Figure, the amount of Cr and Mo increases as LMP increases and in the beginning stage, the amount of Cr and Mo almost remains the same but as the degradation progresses, the amount of Mo gradually increases. This trend has been commented in other papers.[6] That is, steel containing of Cr and Mo produce the carbide composed with Cr and Mo because they are serviced under elevated temperature. In addition, if the degradation continuously progresses, the element Mo of Carbide finally dominates the element Mo_6C of Carbide.[5)-6)]

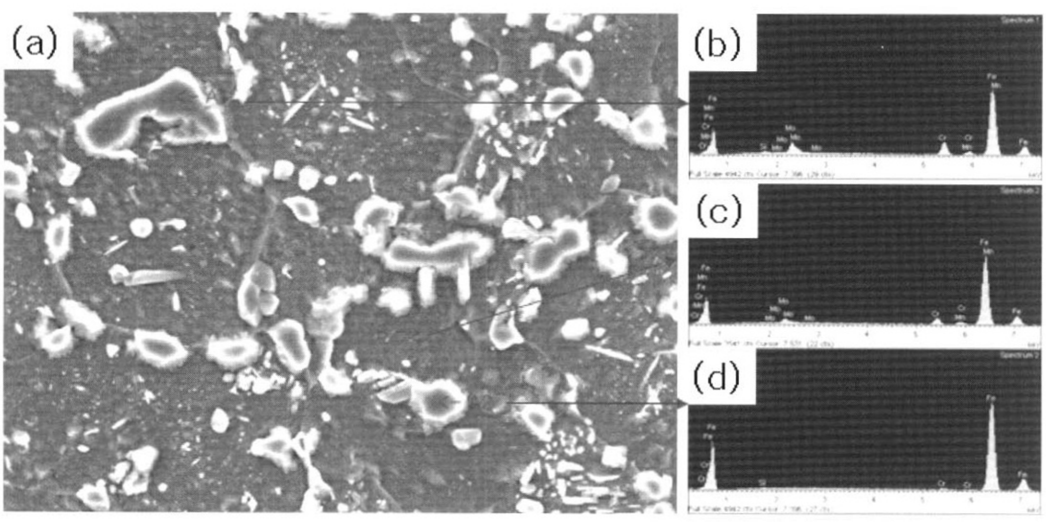

Fig. 4. SEM and EDX analysis on the ruptured reheater tube
(a) microstructure at thickness reduction part, (b) EDX analysis on the carbide in grain boundary,
(c) EDX analysis in matrix, (d) EDX analysis on the carbide in grain boundary,

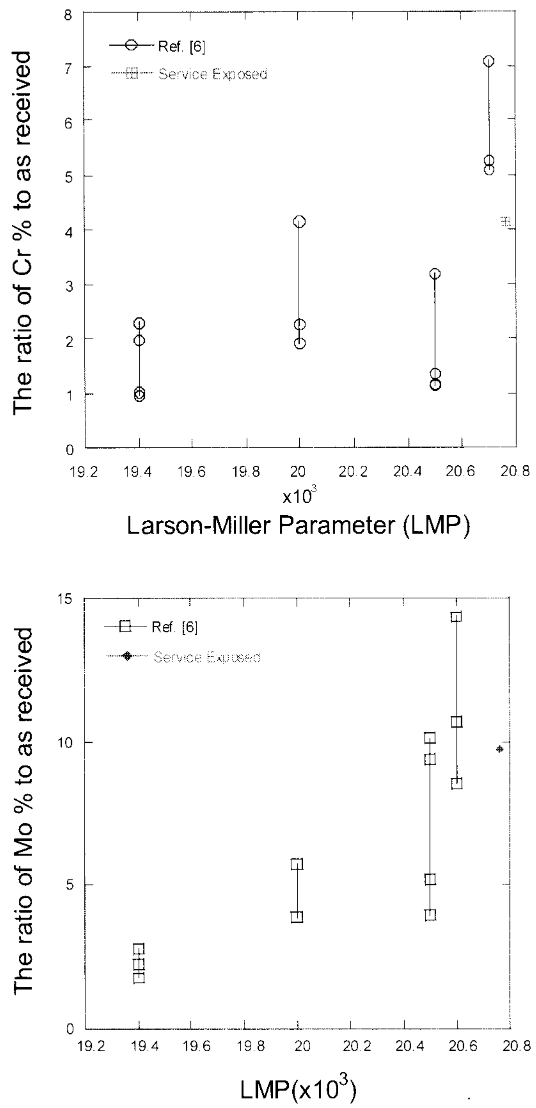

Fig. 5. The weight percent ratio of Cr and Mo in carbide with respect to new material.

Thus, the amount of solid solution reinforcement elements in the grain decreases, the material accelerates, and consequently elements Cr and Mo in carbide become the primary cause declining the mechanical intensity.[5] Considering that the operation time of the boiler tubes is 151,000 hours under 540 ℃, the LMP value becomes 20,470. In the ruptured tube, considering the amount of Cr and Mo, the degradation progress more than that of material operated under the design temperature(540 ℃).

3.3 Tensile test and hardness test

As mentioned in the previous sections, we can identify the primary cause of corrosion and degradation of the tubes, leading into decrease of the amount of solid solution reinforcement elements in the grain, accelerated ductility, and declination of mechanical intensity through the tensile test and hardness test results. In detail, hardness measurement shows 176 Hv for new material and 130 Hy for degraded material. The hardness value is considerably low than the pre-assumed hardness values (LMP: 20470) with the same operation hours (151,000 hours) and the designed temperature (540 ℃) considering the hardness master-curve shown in the previous research.[6] In order to Figure out strength declination in degraded materials, we measure mechanical strength in the room temperature. As a result, yield strength is 290 MPa, tensile strength 490 MPa, and elongation 18%. The strength is approximately declined over 20 MPa compared with the strength(520MPa) which is based on the tensile strength maste-curve of the previous research[6] for 151,000 operation hours under the 540 ℃. This means that the facilities have been operated excessively. it is considered that the overall degradation of the boiler tube materials has considerably been progressed

4. Conclusion

The different types of experiments were carried out, such as structure inspection, hardness measurement and high temperature tensile test on 2.25 Cr-1Mo steel used for the boiler tubes in fossil power plant. The conclusions are as follows:

1) Scale layers caused by oxidation are formatted in the inner parts and outer parts of the tubes. These corrosion layers continuously become expanded irregularly as operating time goes and the thickness of fresh part more decreases. Eventually, the local rupture occurs on the corrosion regions.

2) it was shown that carbide got coarsened both in the grain and grain boundary in ruptured tube. The amount of Cr and Mo in carbide increased in accordance with the progress of the degradation.

3) Tensile strength and Hardness strength are relatively lower than new material and mechanical strength and hardness decreased in accordance with the progress of degradation.

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