High-temperature corrosion behavior of high-temperature and high-pressure cavitation processed Cr–Mo steel surface

Masataka Ijiri a,*, Takayuki Ogi b, Toshihiko Yoshimura b

a Tokyo Denki University, 5 Senju-Asahi-Cho, Adachi-Ku, Tokyo, 120-8551, Japan
b Sanyo-Onoda City University, 1-1-1 Daigaku-Dori, Sanyo-Onoda, Yamaguchi, 756-0884, Japan

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ABSTRACT

In this paper, long-term high-temperature corrosion at 500 °C and high-temperature corrosion at the melting temperature of a corrosive ash mixture were examined because the use of high-temperature equipment such as boilers and gas turbines increases year over year. To investigate the optimum cavitation processing conditions for the specimens used in high-temperature corrosion tests, the surface properties of each processed specimen were examined. In specimens processed using multifunction cavitation (MFC), the compressive residual stress was high when the processing time was 10 min and the Cr content on the surface was greater than on the surface of an unprocessed specimen. On the other hands, in specimens subjected to water-jet peening (WJP), the compressive residual stress was high when the processing time was 10 min. In the present study, the processing time was selected to be 10 min and all high-temperature corrosion tests were conducted by the coating method. In the case of long-term high-temperature corrosion at 500 °C, the corrosion loss of the MFC-processed and WJP-processed specimens was small, whereas the corrosion loss of the unprocessed specimen was large.

1. Introduction

High-temperature corrosion is a general term for chemical damage that occurs in high-temperature environments where various gases and fuel ash are present; “high-temperature corrosion” refers to corrosion damage that occurs in a single state or coexists with phenomena such as oxidation, sulfuration, carburization, decarburization, and nitriding. Fossil fuels used as fuels for high-temperature equipment such as aircraft engines, gas turbines, and boilers contain a certain amount of sulfur as impurities. The sulfur leads to the production of gaseous sulfur compounds such as H2S, SO2, and SO3 at the time of combustion and affects the high-temperature corrosion of the metals in equipment. However, high-temperature equipment is not only corroded by gas components but also suffers remarkable corrosion damage due to the adhesion or deposition of combustion ash.

In recent years, corrosion damage due to the adhesion or deposition of combustion ash has become a serious obstacle to achieving high-efficiency and long life of high-temperature equipment. Notably, in high-temperature environments, in addition to material properties such as creep deformation, creep rupture, thermal fatigue, and low cycle fatigue, material aging is also a problem because it leads to mechanical properties decreasing more than expected in corrosive environments. Recently, several techniques have become available for improving corrosion resistance, such as plasma nitriding [1] and ceramic coating [2] of the surface of low-alloy steel. However, all involve the formation of a compound film on the surface, and there is a problem with cost.

In a previous report [3], under the assumption of high-temperature operation of boilers and reaction vessels, a surface treatment was applied to low alloy steel (Cr–Mo steel) using water-jet peening (WJP) [4, 5, 6] or multifunction cavitation (MFC) [7, 8, 9] technology and the corrosion behavior of the treated steel at 500 °C was examined. The approach proposed in the present research does not form a compound on the surface, but uses the oxide film formed by processing to prevent high-temperature corrosion at 500 °C. In the high-temperature corrosion experiments of specimens coated with a sulfur-based component (K2SO4–Na2SO4), the MFC-processed specimen showed less corrosion loss than the WJP-processed specimen and an unprocessed control specimen. The MFC processing formed a protective film on the surface of
the specimen, and almost no rusting [10, 11, 12] occurred even for several months after processing compared with the WJP-processed surface. The surface potential of the MFC-processed specimen is higher than that of the WJP-processed specimen and the unprocessed specimen, and an oxide film is formed on the surface after treatment. Improved corrosion resistance has also been demonstrated in Ni–Cr–Mo steel [16] and Al–Cu alloy [13]. This decrease in corrosion loss has been reported to be related to the application of compressive residual stress, among other factors [14]. In addition to cavitation processing, other technologies for applying compressive residual stress to material surfaces include shot peening [15, 16, 17, 18]. When compressive residual stress is applied to the material surface, it suppresses cracking that is likely to occur because of thermal stress induced by high-temperature corrosion.

Frequency of use of high-temperature equipment such as boilers and gas turbines continues to increase on a yearly basis. Thus, in the present study, we investigate long-term high-temperature corrosion at 500 °C under a high-temperature environment and high-temperature corrosion above 500 °C.

2. Experimental methods

2.1. Test material and processing conditions

The test material was Cr–Mo steel, which is a material used in mechanical structures. Its chemical composition is shown in Table 1. After solution heat treatment of the steel at 860 °C for 1 h, it was quenched in oil. The specimen was tempered at 550 °C for 2 h and then quenched in water before being cut into 45 × 45 × 5 mm³ specimens for use in experiments. The specimen used for the high-temperature corrosion tests was 30 × 30 mm², which is a small surface area that is necessary due to the processing range of WJP and MFC.

WJP and MFC were performed in the same way as in the previous study [3]. In addition to the aforementioned processing techniques, a swirl flow nozzle (SFN) [19, 20] was installed to increase the number and size of cavitation bubbles at the tip of the WJ nozzle. Attaching an SFN has been demonstrated to enable suppression of erosion traces formed in the central part when an Al surface is processed [19, 21]. The inclusion of an SFN also reduces the extent of surface damage caused by cavitation bubbles that form around erosion traces. The processing times were 2, 10, 20, and 30 min.

2.2. Selection of high-temperature corrosion conditions

The coating test was used as the corrosion test method, and the weight ratio of the mixed ash of K₂SO₄ and Na₂SO₄ was 1:1. The melting point of this synthetic ash was 870 °C or greater according to the K₂SO₄–Na₂SO₄ phase diagram [22]. The high-temperature corrosion was performed at 500 °C and 890 °C (i.e., above and below the melting temperature of the K₂SO₄–Na₂SO₄ mixture) in an electric furnace. After the specimens were maintained at approximately 500 °C for 48 h, 96 h, 144 h, or 192 h, they were air-cooled. Because corrosion progress remarkably at approximately 890 °C (near the melting point), after the specimens were heated from room temperature to 890 °C, they were removed from the electric furnace and the high-temperature corrosion cycle test was performed separately at 890 °C. This high-temperature corrosion cycle was carried out ten times. To monitor the time at which the specimen surface temperature was 890 °C in the electric furnace and the time required for it to air cool to room temperature after removal from the electric furnace, a thermocouple was spot welded onto the specimen surface. An electric furnace was heated to 890 °C, and the specimen was heated within until its temperature reached 890 °C, at which point the specimen was removed from the furnace and air cooled. Figure 1 shows the relationship between the time required to reach 890 °C and the time at the air-cooled temperature. The temperature reached approximately 890 °C in 13 min 16 s, and the time required for the specimen to cool to room temperature after being removed from the furnace was 1 h 15 min, which was adopted as the condition of high-temperature corrosion.

The high-temperature corrosion cycle tests were also performed during the coating tests. The coating test was performed in the same way as in the previous study [3]. This test was performed 10 times.

2.3. Evaluation methods

Residual stress was performed in the same way as in the previous study [3]. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDS, JSM-7100F, JEOL, Ltd.) was used to observe the surface. Composition analysis in the depth direction of the oxide film was carried out using Marcus-type glow-discharge optical emission spectroscopy (GD–OES, GD-Profiler 2, Horiba, Ltd.). During measurements, the Ar gas pressure was 600 Pa and the high-frequency output was 35 W.

3. Results and discussion

3.1. Selection of optimum processing conditions for specimens used in high-temperature corrosion tests

To investigate the optimum processing conditions for the specimens used in high-temperature corrosion tests, the surface properties of each processed specimen were investigated. Figure 2 shows the specimen surface after (a) MFC and (b) WJP processing. An oil-based ink was applied to the specimen surface in advance to identify the location of the peening before processing. After processing, when the peeling condition of the ink was observed, compared with WJP, MFC expanded the peeling range of the ink by ultrasonic irradiation and also influenced the peening distribution. At 2 min, no change was observed on the surface after MFC processing. However, at 20 min, the color of the surface became yellow; at 30 min, many yellow-colored products were generated. However, when the specimen was processed for 2 min with WJP, a slight yellowish-colored product was generated, but the amount of product gradually increased with increasing processing time. This product was considered to be rust in a previous report [11]. With respect to the occurrence of rust, it is considered have speculated that extensive rust is generated due to

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Table 1. Chemical composition of the Cr–Mo steel used in the experiments (mass%).

| C   | Si  | Mn | Fe | Cr | Mo | Ni | P   |
|-----|-----|----|----|----|----|----|-----|
| 0.38| 0.25| 0.82| 0.019| 0.002| 1.18| 0.19| Bal.|
dissolved oxygen [10, 12, 14] generated during processing attaching to the surface. In addition, compared with the rust generation rate on the surface processed with MFC, that on the surface processed with WJP is lower. We attribute this result to a corrosion-resistant oxide film formed on the surface of the WJP-processed specimen. Interestingly, in a previous report [14], the surface potential of an MFC-processed Cr–Mo steel surface was found to increase and its corrosion resistance was confirmed to have improved. However, the corrosion resistance decreased because the surface potential decreased when the processing time was greater than 20 min.

To investigate the elemental composition of the aforementioned film, we studied its Cr component. Cr is one of the elements that improve corrosion resistance in steel materials. In fact, the corrosion resistance of stainless steel results from a high concentration of Cr that leads to the formation of a Cr oxide film on the surface of the material. The low-alloy steel used in the present work is an alloy to which a small amount of Cr has been added to impart the alloy with surface corrosion resistance better than that of carbon steel.

To investigate the Cr component of each processed outermost surface, we analyzed the surface in the depth direction by GD-OES, as shown in Figure 3. Specifically, Figure 3(a) shows that at 10 min of processing, the amount of Cr in the MFC-processed specimen surface is greater than that in the unprocessed specimen surface. However, the Cr content decreased on the specimen surfaces processed for 2, 20, and 30 min. As shown in Figure 3(b), the Cr concentration on the outermost surface of the WJP-processed specimens was lower than that on surface of the unprocessed specimen at all processing times. These results indicate that the best-performing MFC-processed specimen was obtained with a processing time of 10 min and contained a large amount of Cr on its outermost surface, resulting in the formation of a passive film on the processed surface. However, when the processing time was 20 min or more, the rust formed on the surface is assumed to have formed after processing as a result of Cr in the steel dissolving in water after the passive film formed at 10 min was torn. In addition, diffusion-decarburization [14] has been reported to occur on MFC-processed Cr–Mo steel surfaces because of a decrease in surface hardness and the conversion of pearlite to ferrite at long processing times.

To investigate the C component of each processed outermost surface, the surface in the depth direction was characterized by GD-OES; the results are shown in Figure 4. In the specimen processed by MFC...
(Figure 4(a)), the C on the outermost surface of specimens processed for each time was greater than that on the outermost surface of the unprocessed specimen. These results indicate that the temperature inside the cavitation bubble generated by MFC increased and that, when the bubble collided with the surface, the surface temperature increased and the C diffused to the outermost surface. As the processing time increases, the amount of C on the outermost surface decreases. We speculate that, as the processing time becomes longer, C, like Cr, dissolves in water, where it combines with dissolved oxygen, leading to the exhaustion of gases such as carbon monoxide and carbon dioxide. In the case of the WJP-processed specimen (Figure 4(b)), similar to the case of the MFC-processed specimen, the amount of C on the outermost surface was greater than that on the surface of the unprocessed specimen. The increase in the C content is slower than that after MFC processing, and the C content tends to increase gradually with increasing processing time.

The aforementioned results are attributed to the high mechanical energy in the cavitation bubbles generated by WJP, which results in a slight increase in the temperature of the outermost surface when the bubbles collide with the specimen surface. We therefore considered that the C content gradually increased at the outermost surface without decarburization. An increase in water temperature during WJP processing has been reported previously [10, 12, 13], whereas an increase in surface temperature has not.

Cracks, which are likely to occur because of high-temperature corrosion, have been reported to form on surfaces subjected to compressive residual stress [3]. We therefore investigated the residual stress on each of the processed surfaces at each time (Figure 5). Before processing, the specimens’ surfaces were subjected to strong grinding to confirm the effect of each processing method. We confirmed that compressive residual stresses of −53.77 MPa and −214.19 MPa were applied in the grinding direction (Figure 5(a)) and in the direction perpendicular to the grinding (Figure 5(b)), respectively. The compressive residual stress in the grinding direction of the specimen processed by MFC was small at 2 min, reached the maximum value at 10 min, and decreased at 30 min. In the case of the WJP-processed specimen, the compressive residual stress was small at 2 min, similar to that of the MFC-processed specimen, but reached its maximum at 10 min and decreased at 20 min. The compressive residual stress in the direction perpendicular to the grinding direction of the specimen processed by MFC was small at 2 min, reached the maximum value at 10 min, and decreased gradually with increasing time. The value of the residual stress hardly changed in the WJP-processed specimen; however, the value of the residual stress in the direction perpendicular to the grinding direction decreased slightly as the processing time was extended. The change in the residual stress in the measured direction on each processed surface was attributed to the grinding direction before processing. We speculated that when the tensile residual stress is applied before processing, compressive residual stress is more likely to be applied via the shake-down effect than on the surface where no tensile residual stress is applied. From these results, the processing time of the specimen used for high-temperature corrosion was set to 10 min.

Figure 6 shows the state of compressive residual stress of specimens treated in an electric furnace at 500 °C before hot corrosion at 500 °C for an extended period. The residual stress was measured in the grinding direction.
direction, where the compressive residual stress was applied most. The residual stress of the unprocessed specimen was approximately 0 after 48 h. For specimens subjected to MFC or WJP processing, the compressive residual stress decreased rapidly at 48 h and became constant at 96 h or more. The specimen subjected to MFC processing exhibited a slight residual compressive stress even when it was heated for a longer time than the specimen processed by WJP.

3.2. High-temperature corrosion behavior of specimens heated at 500 °C for an extended period and at the melting temperature of corrosive ash

Figure 7 shows the corrosion weight loss of a specimen corroded at 500 °C. The specimens subjected to MFC and WJP processing exhibit smaller corrosion losses than the unprocessed material. The corrosion loss was low in the specimen processed by MFC because the passive film was formed on the surface after processing. However, as shown in Figure 3, the outermost surface of the specimen processed by WJP contains less Cr than the surface of the unprocessed material; thus, almost no passivation film was formed. The low corrosion weight loss is likely related to the compressive residual stress applied to the surface. We speculate that this compressive residual stress suppresses stress corrosion cracking and voids that are likely to occur inside by delaying the time to change to tensile stress caused by the temperature difference between the surface and inside during heating. In fact, the compressive residual stress has been reported [3] to prevent voids, which easily occur inside the specimens. However, the effect of this compressive residual stress on the surface is not clear; this issue should be addressed in detail in future studies.

Figure 8 shows the cross section of the specimens processed by MFC after hot corrosion at 500 °C for 192 h. Gray indicates the metal microstructure, while white indicates corrosive ash. O, K, and S elements were observed in the corrosive ash. Around the corroded ash, shading was observed by elemental mapping of Cr, suggesting that the passivation film suppresses the propagation of high-temperature corrosion. In the unprocessed material and the specimen processed by WJP, a few spots were observed where corrosive ash remained (Figure 8); in the specimen processed by MFC, numerous such spots were observed.

Figure 9 shows a cross section of the unprocessed specimen after hot corrosion at 500 °C for 192 h. Some spots similar to those in Figure 8 were observed; however, in this case, the corrosive ash progressed from the surface in the thickness direction in some areas (Figure 9). In the areas surrounding the regions where corrosion is progressing, the density of Cr is lower, as revealed by elemental mapping images. The elemental mapping image of S confirms a location where the corrosive ash clogged the specimen surface in the thickness direction; an enlargement of the area around it (broken line) confirms the presence of voids (Figure 10). In the specimen processed by MFC and that processed by WJP, corrosive ash regions like those in Figure 9 were not observed. These results indicate that a barrier of Cr film and compressive residual stress are necessary to protect the outermost surface from corrosive ash. When no compressive residual stress is applied to the outermost surface, corrosion from the surface to the thickness direction tends to be accelerated.

Figure 11 shows the corrosion loss as a function of the number of cycles of high-temperature corrosion at the melting point temperature of
the corrosive ash. The corrosion weight loss of unprocessed materials was low, whereas that of specimens processed by WJP and MFC was high. WJP or MFC processing likely formed a passivation film on the specimen surface; after the passivation film formed on the surface was torn, the internal Cr content became deficient, promoting corrosion from the surface. However, the mechanism by which the WJP- and MFC-processed specimens exhibit greater corrosion weight loss than the untreated specimen could not be clarified at this time.

The aforementioned results show that MFC or WJP processing of Cr–Mo steel effectively improved the steel's corrosion resistance in long-term high-temperature corrosion tests but was not effective at temperatures near the melting temperature of corrosive ash. On the surface of the Cr–Mo steel, the formation of a passivation film and the application of compressive residual stress on the outermost surface are speculated to suppress the progression of high-temperature corrosion at 500 °C.

4. Conclusions

- Rust was generated on the surface of Cr–Mo steel specimens subjected to MFC when the processing time was longer than 20 min, and rust formed on the surface of specimens processed by WJP when the processing time was longer than 2 min. The formation of this rust depends on the amount of Cr in the outermost surface after processing, and the Cr content of the surface processed by MFC for 10 min clearly increased. In addition to the Cr content, the C content of the surface also increased. These results indicate that the temperature inside the cavitation bubbles generated by MFC increases and that the temperature of the specimen surface increases.

- On the surface of specimens subjected to MFC or WJP, the greatest compressive residual stress was applied when the processing time was 10 min. The compressive residual stress of each processed surface was slightly higher than that of the unprocessed material heated in an electric furnace at 500 °C for an extended period. A passive film likely formed on the surface after each process.

- As a result of high-temperature corrosion at 500 °C for an extended period, the corrosion weight loss of the MFC-processed and WJP-processed specimens was small and the corrosion weight loss of the unprocessed specimen was large. These results are attributed to the compressive residual stress applied to the surface. The cross section of the outermost surface was analyzed by SEM–EDS, and the results...
suggested that a Cr oxide film on the surface also effectively protects the surface from corrosive ash.

During high-temperature cycling near the melting point of the corrosive ash, the MFC-processed and WJP-processed specimens exhibited the greatest corrosion weight loss and the unprocessed specimen exhibited the smallest corrosion weight loss. The surfaces subjected to WJP or MFC tend to form a nonmoving body film on the surface after the treatment, resulting in Cr becoming easily deficient inside the specimen. Therefore, we speculated that, when the nonmoving body film formed on the surface peels off, the corrosion from the surface tends to progress remarkably.

Declarations

Author contribution statement

Takayuki Ogi: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Masataka Ijiri: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Toshihiko Yoshimura: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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