Improvement of corrosion resistance of low-alloy steels by resurfacing using multifunction cavitation in water

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Abstract. Low-alloy steels are based on carbon steel in combination with several percent or less (in many cases, 1 mass%) alloying elements, and they offer improved resistance to corrosion at a cost slightly higher than that of carbon steel. However, these materials do not exhibit the same corrosion resistance as stainless steel. The authors have previously developed a novel multifunction cavitation (MFC) technique, which combines ultrasonic cavitation with water jet cavitation. In this study, MFC was used to modify the surface of Cr-Mo steel (SCM435) and Ni-Cr-Mo steel (SNCM630). MFC was found to improve the residual stress value of the material as the result of surface modification while also imparting high strength and superior corrosion resistance.

1. Introduction

Low-alloy steel is based on carbon steel combined with several alloying elements, such as Ni, Cr, and Mo, in an amount of several mass% or less (in many cases, 1 mass% or less). Different types of low-alloy steels are made for various applications: heat-resistant steel, low-temperature steel, weather-resistant steel, and high tensile-strength steel. This steel costs slightly more than carbon steel but has better corrosion resistance. However, the corrosion resistance of low-alloy steel is inferior to that of stainless steel. In low-alloy steel, rust formation is prevented by two methods. Firstly, the surface can be covered by paint or plating. Secondly, the alloy contains Cu, Cr, P, and Ni, which are corrosion-resistant alloying elements. In appropriate amounts, these alloys encourage the formation of a dense rust on the surface as the steel is exposed to alternating moderate dry and wet conditions in the atmosphere over time. This dense rust protects the underlying steel material, and the formation of deeper rust is gradually suppressed. However, elements effective for improving corrosion resistance are harmful to the excellent mechanical properties and good weldability. Low-alloy steel is required to have. As a result, there is a limit to the amount added, and a limit to the corrosion resistance that can be “built in” to the alloy mixture.

The authors developed a new water jet cavitation (WJC) technology [1]. This technique is a mechanical and electrochemical cavitation method because it has electrochemical action by a high-temperature reaction field of ultrasonic cavitation (UC) in addition to mechanical action by high-pressure microjets (MJs). Furthermore, it can be called multifunction cavitation (MFC) because it combines new functions when processing the surface of various materials. In this technology, various material properties have been studied so far. Previously, the authors reported that TiO₂ powder, which is widely used as a photocatalytic material, can be fabricated at the nanoscale when processed with MFC [2]. In addition, in an indium tin oxide (ITO) film, which is applied to the transparent electrode mounted on liquid crystal displays, when the ITO film coating on a transparent electrode is subjected to MFC...
treatment, indium, which has a low melting point, can be melted and released [1]. This phenomenon demonstrated that MFC heats the specimen surface to a high temperature in water.

In the present study, MFC was applied to the modification of low-alloy Cr-Mo steel (SCM435) and Ni-Cr-Mo steel (SNCM630) surfaces. Then, we investigated the effect of MFC on the alloy microstructure and hardness and compared the results to alloys processed with WJC.

2. Experimental methods

The material used for these tests was Cr-Mo steel (SCM435) and Ni-Cr-Mo steel (SNCM630), both structural steels, the chemical compositions of which are shown in Table 1.

Table 1. Chemical composition of the low-alloy steels used in this work (mass%).

|       | C   | Si  | Mn  | P   | S   | Ni  | Cr  | Mo  | Cu  | Fe  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| SCM435| 0.37| 0.32| 0.81| 0.014| 0.012| 0.012| 0.95| 0.15| 0.14| Bal.|
| SNCM630| 0.29| 0.24| 0.44| 0.11 | 0.018| 2.93 | 3.01| 0.56| 0.03| Bal.|

Figure 1 is a schematic diagram of the equipment used for MFC processing. In conventional WJC apparatus, a nozzle is fixed in water at room temperature and water jets are pumped through it at a discharge pressure of 35 MPa. The nozzle diameter was 0.8 mm. The distance between the nozzle and the specimen was 65 mm. The size of the water tank was 60×45×37 mm³, and it was filled with tap water. In MFC treatment, an ultrasonic transducer is placed next to the water jet nozzle for conventional WJC, and ultrasonic waves are propagated to the water jet flowing from the nozzle. The ultrasonic wave had an output of 225 W and frequency of 28 kHz.

As shown in Figure 2, bubbles from WJC isothermally expand when the sonic pressure due to ultrasonic irradiation exceeds the Blake threshold, and after the bubbles expand to a certain size, Rayleigh shrinkage occurs rapidly (adiabatic compression). The flow cavitation, including the hot spot, becomes MFC by the repetition of isothermal expansion and adiabatic compression. At the same time that the MFC begins to collapse, it approaches the specimen surface.
Figure 2. Multifunction cavitation mechanism.

Figure 3 shows the bubble shape change from photographs taken by a high-speed camera during bubble collapse into an aspheric shape [3]. As the volume of the bubble decreases, a MJ with a columnar shape is formed and impinges on the specimen surface. This phenomenon is referred to as micro-forging because the MJ provides high-temperature and high-pressure processing in a microscopic area. Conventional WJC produces large high-pressure bubbles (diameter of several hundred micrometers at approximately 1,000 MPa), whereas bubbles produced with conventional UC are small (several micrometers) with high temperature (several thousand degrees Celsius). In contrast, the MJ that occurs in a bubble during MFC is a deforming liquid-phase body similar to a liquid jet (column) at the terminal stage of bubble collapse, and the interior temperature and pressure of the bubble become high (several thousand degrees Celsius and approximately 1,000 MPa, respectively). The processing time for all three methods was 2 min. Residual stress was measured by the full-width at the half-value breadth method from the (211) lattice spacing strain using Cr Kα X-ray diffraction (MSF-3M, Rigaku Corporation). Micro Vickers hardness tests were performed at room temperature under a load of 1.96 N for 10 s. The hardness values were averaged from eight measurements after the minimum and maximum of ten measurements were discarded.

Figure 3. Images showing the aspherical collapse of a bubble at time intervals of (a) 0-163 μs and (b) 165-169 μs.
In addition, hardness measurements near the surface after processing were performed after slight mechanical polishing to remove the oxide film and peening marks formed during processing. Microstructure observations were conducted using optical microscopy (OM) and scanning electron microscopy (SEM; S-4800, Hitachi). Before observation, the specimens were etched in 5 vol% Nital. The specimens used for all analyses after processing were cut to 1×1 cm². For dissolved oxygen (DO) measurement, a portable type DO analyzer (OM–71, Horiba, Ltd.) was used. This measurement was carried out by appropriately collecting treated water in which cavitation occurred within a reactor made of SUS304 for a processing time of 30 min.

3. Results and discussion

Table 2 shows the results of residual stress measurements. To further increase the compressive residual stress generated after WJC and MFC processing, the specimen surface was first subjected to hard grinding, which imparted tensile residual stress by a shakedown effect. These measurements were conducted in a state without rust on the specimen surface just after each processing and were performed in a direction parallel to the grinding direction. It was confirmed that grinding imparted a tensile residual stress in the grinding direction of the unprocessed specimens, while a compressive residual stress was imparted in the vertical direction. In WJC and MFC processing, compressive residual stress is generated when the specimen surface is compressed by the pressure from cavitation because the MJ applies force in the lateral direction, leading to plastic deformation around the region that is elastically constrained by its surroundings.

Table 2. Compressive residual stress of specimens before and after various treatments (MPa).

|                  | SCM435 | SNCM630 |
|------------------|--------|---------|
| **As received**   |        |         |
| after grinding    |        |         |
| **Vertical**     | -173   | -238    |
| **Parallel**     | +202   | +155    |
| **UC**           | -216   | -196    |
| **WJC**          | -361   | -450    |
| **MFC**          | -293   | -481    |

Figure 4 shows the change in the micro Vickers hardness for each processed surface in the depth direction but does not include the oxide film and peening marks. In the hardness of the near-surface region in the unprocessed specimen, SCM435 was 246 HV and SNCM630 was 256 HV. The hardness distribution of the unprocessed specimen remained unchanged in the depth direction. Thus, the surface grinding did not significantly influence the hardness of the unprocessed specimens. The hardness in the near-surface region of the WJC-processed SCM435 was 271 HV. The hardness decreased at a depth of about 0.75 mm from the surface. On the other hand, the hardness in the near-surface region of the MFC-processed specimen was 276 HV. The hardness decreased at a depth of about 0.5 mm from the surface layer. This hardness change depends on the value (compressive stress field) where compressive residual stress was added in the depth direction. The compressive stress field was deeper in the WJC specimen than in the MFC specimen. The compressive stress field occurred at a depth of about 0.5 mm after WJC processing, and it occurred at a depth of about 0.25 mm after MFC processing. At a depth of about 0.50 mm in the WJC-processed specimen, the hardness decreased compared with the abrasive material due to voids and cracks. The influence of voids and cracks inside the specimen is thought to be the reason why the hardness decreased from a depth of about 0.5 mm in the specimen after WJC processing. Recently, the authors reported that voids and cracks tend to form inside the specimen after WJC processing [4]. The hardness in the near-surface region of the WJC-processed SNCM630 was 270 HV. The hardness decreased at a depth of about 1.00 mm from the surface. On the other hand, the hardness
in the near-surface region of the MFC-processed specimen was 264 HV. The hardness decreased at a depth of about 1.00 mm from the surface. The compressive stress field occurred at a depth of about 0.75 mm after WJC processing, and it occurred at a depth of about 0.50 mm after MFC processing.

**Figure 4.** Hardness depth profile of the specimens after WJC and MFC treatment: (a) SCM435 and (b) SNCM630.

Figure 5 shows surface photographs of SCM435 (a, b) and SNCM630 (c, d) specimens after processing. The specimen surface was painted with oil-based ink prior to processing to identify the peening positions. The condition of the ink coating showed that the diameter of the peened portion of SCM435 was 40.8 mm after WJC processing and 42.2 mm after MFC processing. The peened diameter of SNCM630 was 41.3 mm after WJC processing and 42.7 mm after MFC processing. Therefore, MFC produced a slightly larger area than WJC produced. In addition, when the processed specimens were kept at room temperature for several months, corrosion developed after WJC processing, whereas there was almost no corrosion after MFC processing. Perhaps corrosion of the SNCM630 steel was prevented due to the formation of a dense oxide film on the specimen by increased temperature on the surface.

**Figure 5.** Surface change after treatment: of (a, c) WJC and (b, d) MFC. (a) and (b) are SCM435 and (c) and (d) are SNCM630.
Figure 6 shows OM micrographs of the SCM435 specimens after (a) WJC and (b) MFC. The particle size in the depth direction from the surface after each process was not significantly affected. In the near-surface region, no significant corrosion was observed after WJC processing, although it occurred easily after MFC processing. Corrosion was not observed in the ferrite phase but in the pearlite phase. The rust formed to a significant extent from the surface to a depth of approximately 1 mm.

![Figure 6. Optical micrographs of the SCM435 depth profile after (a) WJC and (b) MFC. A dotted line indicates a specimen surface.](image)

Figure 7 shows SEM micrographs of the SNCM630 specimen depth profiles after WJC and MFC. The particle size in the depth direction from the surface after each process was not significantly affected. In the near-surface region, no significant corrosion was observed after WJC processing, although it occurred easily after MFC processing. Thus, selective oxidation is considered to have occurred in the bulk of the MFC-processed specimen. The element that is difficult to oxidize in this specimen is Cr, which migrates to the topmost surface and forms a Cr-poor region beneath the surface during heating by MFC processing. As a result, rust can be easily generated because the amount of Cr decreased in the near-surface region.

![Figure 7. SEM images of the SNCM630 depth profile after (a) WJC and (b) MFC. A dotted line indicates a specimen surface.](image)
The corrosion resistance of the specimen surfaces was assessed by measuring surface potentials, and the results are summarized in Table 3. The work function corresponding to the surface potential decreases as the surface roughness increases. The cavitation at the material surface during WJC generates impact pressures greater than several thousand megapascals. In addition, because some thermal energy is transferred to the material surface, a passive (corrosion-resistant) layer is formed. Soyama et al. [5] have also reported the formation of a passive layer as part of the mechanism by which the corrosion resistance of carbon steel is improved following the application of a cavitation jet. Regarding SNCM630, the surface potential of the WJC-processed specimen was lower than the abrasive material. It is probably influenced by the increase in surface defects compared with SCM435. During MFC, the bubbles generated by WJC (which are larger than UC bubbles) are irradiated with ultrasonic waves, and thus possess both high temperature (several thousand degrees Celsius) and high pressure (approximately 1,000 MPa). As these bubbles collide with the surface, a more stable passive layer is formed than that obtained with WJC.

### Table 3. Surface potential of specimens after various treatments (mV).

|       | SCM435 | SNCM630 |
|-------|--------|---------|
| As received | 234 ± 14 | 359 ± 25 |
| UC | 194 ± 13 | 342 ± 18 |
| WJC | 382 ± 26 | 329 ± 18 |
| MFC | 544 ± 17 | 445 ± 16 |

The reason for the selective oxidation inside the specimen during MFC processing was investigated by monitoring the water temperature, and Figure 8 summarizes the results. While UC did not increase the water temperature, both WJC and MFC did raise the temperature in the reactor. This occurred as a result of the pressurization of the water by the high-pressure pump, because the kinetic energy of the water was converted to thermal energy. From the viewpoint of bubble energy, it is thought that both WJC and MFC generate larger bubble collapse energies than UC processing, which also increases the water temperature. The slightly higher temperature obtained during MFC compared to WJC processing is due to the application of ultrasonic energy, reflecting the hot spots generated in the bubbles.

### Figure 8. Relationship between processing time and underwater temperature.

Figure 9 plots the DO in the reactor over time for each processing method. The DO concentration was almost unchanged during UC, whereas it decreased during both WJC and MFC processing. In WJC processing, the pressure applied to the specimen surface increases due to the shock wave generated by the MJ. A part of the foam is deformed or bubbles become large again over a very short time span, and
so both the water temperature and the temperature of the processed surface increase. As a result, it is believed that DO combines with Cr to form oxides on the processed specimen surface, causing DO in the water to decrease. During MFC, the bubbles (which have a high internal temperature and pressure) increase the sample surface temperature to a greater extent than during WJC processing due to the hot-spot phenomenon inside the bubbles. Thus, the DO concentration is reduced to a greater degree as a passive layer is generated.

As described above, in the MFC technique, bubbles having characteristically high temperature and high pressure collide with the specimen surface as the result of irradiating large bubbles generated by WJC with ultrasonic waves. This method effectively improves the surface residual stress via surface modification and also increases the specimen strength and corrosion resistance.

4. Conclusion

Improvements in residual stress and surface modification leading to high strength and corrosion resistance were found to occur at the surfaces of specimens processed with MFC. Corrosion resistance was improved via the formation of an oxide film by selective oxidation, as well as the reduction of surface defects. We concluded that this oxide film was formed by dissolved oxygen in the water interacting with Cr on the metal surface during the MFC treatment.

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