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Hydrogen participates in cavitation erosion in water

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ABSTRACT

Pure titanium and 18Mn18Cr0.6 N austenitic stainless steel were selected as model materials to capture hydrogen. Specimens were immersed or exposed to cavitation erosion in ultrapure water. The surface compositions of immersed and eroded specimens were studied using time-of-flight secondary ion mass spectrometry. Throughout the entire sputtering time, the yields of H^- from the eroded specimens were significantly higher than those from the immersed specimens. The hydrogen concentration in eroded specimens had increased. Hydrogen participated in the process of cavitation erosion in water. Finally, the sources of this extra hydrogen, and how it entered the specimen, were discussed.

1. Introduction

Cavitation erosion (CE) is a frequent material degradation phenomenon for components, such as pumps, ship propellers, valves, and pipes, which experience flowing liquid environments [1,2]. In the past few years, the CE mechanisms of titanium alloys [3,4], nickel alloy [5], stainless steels [6,7], low alloy steels [8,9], and coatings [10,11] have been investigated in some detail. There is consensus on the CE mechanism: local pressure fluctuations induce cavity formation; when these tiny bubbles collapse, high-speed microjets and intense shock waves attack the component surface repeatedly and induce damage—including deformation, material removal, and even fracture [12,13]. In corrosive liquids, the CE mechanism is complex because there are interactions between erosion and corrosion. In distilled water, however, CE is believed to be an entirely mechanical effect [14]. Persistent slip bands and striations on the eroded surface of metals indicate that CE is a fatigue process [15–19].

It is well known that fatigue is sensitive to the environment, especially to the presence of hydrogen [20]. However, hydrogen is rarely considered in the investigation of CE [21]. A recent report [22], found that, for ferritic stainless steel, all the cleavage planes on the eroded surface were {100}. For comparison, fatigue cracks grew along random planes in ferrite in air but along only {100} planes in a hydrogen atmosphere [23]. Taken together, these results suggest that hydrogen participates in CE in purified water [22]; however, strong evidence is still lacking. Water contains dissolved hydrogen; in addition, hydrogen may form through the decomposition of water during cavitation. If hydrogen participates in CE, this should be carefully considered when attempting to explain CE mechanisms and design material microstructures with enhanced CE resistance.

In this study, pure Ti (close-packed-hexagonal crystal structure) and a high nitrogen austenitic stainless steel (face-centered-cubic crystal structure) were selected as model materials. High-nitrogen austenitic stainless steels possess excellent mechanical and chemical properties. They have found broad application in many fields where CE is a common materials-degradation phenomenon [19,24,25]. These materials were subjected to CE in ultrapure water and the eroded surfaces were examined. If hydrogen participates in CE, the eroded specimens will capture it, because pure Ti and austenitic stainless steel are able to dissolve a substantial amount of hydrogen.

2. Experimental

The test materials were commercial pure Ti (TA1) with an average grain size of ~25 μ m and 18Mn18Cr0.6 N austenitic stainless steel (annealed at 1050 °C for 10 min) with an average grain size of ~31 μ m. Specimens (Φ 10 \times 4 mm) were machined and ground with 4000 grit abrasive paper. No polishing was conducted after grinding to avoid any possible introduction of hydrogen. The CE tests were conducted on an XOQS-2500 machine in ultrapure water for 8 h. The test specimen (0.5 mm away from the horn tip) was fixed on a specimen holder [5]. The water temperature, amplitude, and frequency were 298 K, 50 μ m, and 20 kHz, respectively [26]. Ground and eroded specimens were examined using a VEECO Contour GT-K1 optical profiler to characterize their

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surface morphologies.

For comparison, some ground specimens were immersed in ultrapure water at 298 K for 8 h without CE to give the "immersed" specimens. Secondary ion emissions from the immersed specimens and eroded specimens were examined by time-of-flight secondary ion mass spectrometry using a TOF-SIMS 5 instrument. The sputter ions were 1 keV Cs⁺, and the sputter area was 500 × 500 μ m. Measurements were conducted using 30 keV Bi⁺ ions and the analysis area was 200 × 200 μ m. The negative-ion mode was used to give a higher yield of hydrogen ions [27].

3. Results

Fig. 1 shows the surface three-dimensional (3D) morphologies of pure Ti and 18Mn18Cr0.6 N steel specimens. After 8 h CE, material removal was clearly apparent in both materials, and the scratches had been removed. The Ra values of immersed pure Ti and 18Mn18Cr0.6 N steel specimens were 0.968 μ m and 0.498 μ m, respectively. The roughness worsened due to CE.

Fig. 2a and b shows 3D render overlays of H⁻, TiH⁻, and TiO₂⁻ ions for the immersed and the eroded pure Ti specimens, respectively. The top surface of the hexahedron corresponds to the specimen surface, while the side surfaces show how the ion distribution changes with depth. The yield of H⁻ in the eroded specimen is clearly higher than in the immersed specimen. The H⁻ intensity is not uniform on the eroded surface; this is because when material is removed, the hydrogen dissolved in it will also be removed. The surface layer of Ti contains a small amount of water [28]. Although H₂O contains hydrogen atoms, the secondary ions produced from H₂O under the negative ion mode are largely OH⁻ and O⁻; with few other ions apparent [29]. Therefore, the H⁻ ions detected in the present work are attributed to primary emission from hydrogen dissolved in the lattice. Of course, if the hydrogen content is beyond the solubility of hydrogen in pure Ti, extra hydrogen will form titanium hydrides, such as Ti_2H and TiH. The yield of TiH^- in the eroded specimen seems to be higher than in the immersed specimen. TiO_2^- ions represent the titanium oxides. In contrast with the situation for the immersed specimen (Fig. 2a), the TiO_2^- distribution is non-uniform in the eroded specimen (Fig. 2b). The distribution of TiO_2^- is opposite to that of H⁻, as indicated by the arrows at specific positions. In other words, the positions that give a high yield of H⁻ are positions with low yields of TiO_2^- . This phenomenon may be caused by the reducibility of hydrogen.

The intensity of each secondary ion is plotted versus the sputter time in Fig. 2c–e. Increasing sputter time corresponds to greater distance from the sample surface. The H⁻ yields for both specimens fluctuated during the first 50 s of sputtering, before becoming steady (Fig. 2c). Throughout the entire sputtering time, the yield of H⁻ from the eroded specimen remained clearly higher than that from the immersed specimen. During the initial ~20 s of sputtering, the yield of TiH⁻ was higher ffig2or the immersed specimen than for the eroded specimen; after that, the yield of TiH⁻ became lower for the immersed specimen (Fig. 2d). For TiO₂⁻ ions, the yield was higher for the immersed specimen during the initial 300s of sputtering (Fig. 2e).

Fig. 3a and b shows 3D render overlays of H^- , FeO_2^- , and CrO_2^- ions for the immersed and the eroded 18Mn18Cr0.6 N steel specimens, respectively. Obviously, the yield of H^- for the eroded specimen is higher than for the immersed specimen, which is similar to the situation in pure Ti. The 3D render overlays of FeO_2^- and CrO_2^- indicate that thin passive films are formed on both specimens. It can be found that the diffusion depth of hydrogen is greater than the thickness of passive film, especially in the eroded specimen. The distributions of FeO_2^- and $CrO_2^$ ions on the surface of the immersed specimen were more uniform than those on the surface of eroded specimen. Throughout the entire sputtering time, the yield of H^- for the eroded specimen is about three times higher than for the immersed specimen (Fig. 3c); the yield of FeO_2^- from the eroded specimen remained lower than that from the immersed



Fig. 1. 3D morphologies of specimens: (a) ground and (b) eroded pure Ti specimens; (c) ground and (d) eroded 18Mn18Cr0.6 N steel specimens.



Fig. 2. 3D render overlay of negative ions for (a) immersed pure Ti specimen and (b) eroded pure Ti specimen; ion distributions versus sputter time: (c) H⁻; (d) TiH⁻; (e) TiO₂⁻.

specimen (Fig. 3d), which may be caused by the higher hydrogen concentration in the eroded specimen. The yields of CrO_2^- are similar for both specimens (Fig. 3e).

4. Discussion

The question arises: why are the hydrogen concentrations higher in the eroded specimens? In Fig. 3a, the H⁻ intensity is high in the surface layer and decreases with increasing depth in the immersed 18Mn18Cr0.6 N steel specimen. This phenomenon means that 18Mn18Cr0.6 N steel absorbs hydrogen in water. In addition, the nonuniform distribution of H⁻ ions on the surface of the immersed specimen indicates that roughness and strain affect the absorption rate of hydrogen (Fig. 3a). The possible answer to above question is that CE improves the hydrogen concentration in the water and enhances the hydrogen absorption rates of 18Mn18Cr0.6 N steel and pure Ti.

The likely sources of the extra hydrogen, and the mechanisms by which it enters the specimen, are schematically shown in Fig. 4. The collapse of cavities is an intense process. Luminescence occurs and the instantaneous temperature is very high, between ~1500 and 30000 K [30,31]. The pressure can be up to several thousand bars [32]. In this intense process, plasma forms [30]. It is reasonable for the water to decompose to produce hydrogen in atomic, ionic, and molecular states. As a result, the hydrogen concentration becomes high around the collapsed bubble in the water. Microjets carry hydrogen and shoot towards the solid surface at speeds of up to ~80–100 m/s [1,32]. This attack leads to deformation in the solid surface layer, with very high strain rates, ranging from ~1000 to 500000/s [32,33]. A high density of

defects, such as vacancies, dislocations, and twins, forms [34,35], which provides more diffusion paths for hydrogen. In addition, the passive film is continuously destroyed during CE, which may also give contribution to the hydrogen absorption rate. Furthermore, cracks on the eroded surface are also considered pathways of rapid hydrogen movement. Therefore, the high content hydrogen in the eroded specimen results from the combined effect of the high hydrogen concentration in the water, the high-speed impact, the high density of diffusion paths in the solid, and the damaged passive film.

In CE, the material-removal process is usually gradual, and involves spalling of tiny pieces (several microns in size) [19,22,35]. Cracks and their tips are also narrow and shallow. Thus, enrichment of hydrogen close to the surface can have a significant effect on this damage process. Hydrogen participation in CE can explain why all the cleavage fractures in CE of ferritic stainless steel are along {100} planes, as mentioned above [22,23]. Additionally, the finding of hydrogen enrichment can explain other phenomena in CE. For metals with a face-centered-cubic lattice, coherent twin boundaries are readily eroded in preference to the random high-angle grain boundaries (RHAGBs) [19]. Interestingly, the diffusion speed of hydrogen is much higher along coherent twin boundaries than it is along RHAGBs [36]. Furthermore, (001)-oriented grains show lower CE resistance than (111)-oriented grains do [37]. Coincidentally, the diffusion speed of hydrogen is higher in (001)-orientated grains than it is in (111)-oriented grains [38]. It is supposed that hydrogen diminishes the CE resistance of coherent twin boundaries and (001)-orientated grains.

The results of this study imply that the effect of hydrogen on the CE resistance should be considered in material selection and



Fig. 3. 3D render overlay of negative ions for (a) immersed 18Mn18Cr0.6 N steel specimen and (b) eroded 18Mn18Cr0.6 N steel specimen; ion distributions versus sputter time: (c) H⁻; (d) FeO₂; (e) CrO₂.



Fig. 4. Schematic illustration of hydrogen enrichment process in eroded specimen.

microstructural design. Reducing the hydrogen diffusion paths, increasing the concentration of hydrogen traps, and decreasing the hydrogen sensitivity of materials are all potential methods to improve the CE resistance. In addition, acidic solutions, salt solutions, and oils are hydrogen-containing substances. Hydrogen could be produced from the decomposition of water or oil under cavitation conditions, or from the hydrogen ions in acid solution. Consequently, the participation of hydrogen in CE should be taken into consideration for these liquid environments.

5. Conclusions

In summary, for both pure Ti and 18Mn18Cr0.6 N steel, the yields of H⁻ from the eroded specimens were significantly higher than those from the immersed specimens throughout the entire sputtering time. This demonstrated that the hydrogen concentration in eroded specimens had increased. Hydrogen participated in the process of cavitation erosion in water.

Credit author statement

Zhenhua Wang: Conceptualization, Investigation, Writing - Original Draft, Writing - Review & Editing, Project administration, Funding acquisition. **Yong Wang:** Methodology, Investigation, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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