Fatigue strength and fracture mechanisms of sprayed steel with different coatings in 3%NaCl solution

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Abstract

Rotary bending fatigue tests have been conducted at room temperature in 3%NaCl solution using specimens of a medium carbon steel (S45C) sprayed different coatings of a ceramic (Cr2O3), cermet (WC-12%Co) and metals (Ni-11%P and Al-2%Zn). Based on detailed observations of the fracture process, the role of sprayed coatings and the fracture mechanisms are discussed.

1 Introduction

Hard coatings can enhance the resistance of metal alloys to wear, oxidation, thermal exposure and corrosion. Of several surface coating techniques, plasma-spraying has many advantages, i.e. it is applicable to any material system and component shape. In engineering applications, coated materials are subjected to service conditions where fatigue strength is critical. However, the role of plasma-sprayed coatings on fatigue properties and the fracture mechanisms, in particular in corrosive environments, have not yet been studied in any great detail.

In the present study, in order to investigate the corrosion fatigue strength of ceramic-, cermet- and metal-sprayed steel (S45C), rotary bending fatigue
tests have been conducted at room temperature in 3%NaCl solution. The results obtained are discussed based on detailed observations of the fracture process.

2 Materials and experimental procedures

Specimens and sprayed coatings
The materials chosen are a medium carbon steel (S45C) sprayed coatings of ceramic (Cr2O3), cermet (WC-12%Co), and metals (Ni-11%P and Al-2%Zn). The chemical composition (wt.%) of the substrate steel is C: 0.45, Si: 0.21, Mn: 0.75, P: 0.026, S: 0.013, Cu: 0.01, Ni: 0.02, Cr: 0.13, Fe: bal. The material with a diameter of 16 mm was heated to 850 °C, held at this temperature for 1h, and then tempered at 600 °C for 1 h. Subsequently, rotary bending fatigue specimens (diameter=8 mm, gauge length=10 mm) were machined. Electropolished specimens, denoted by EP, were used as a reference for comparison with coated specimens.

The spraying condition of the ceramic is given elsewhere [1]. Three different coated specimens were prepared, i.e. TC = top coating (Cr2O3), TUC = under-coating (Ni-5%Al) plus top-coating, and TUCS = sealing of pores contained in the top-coating of TUC specimens. Thermal setting polymer which is commercially available, was used for the sealing treatment. For the TUC specimens, there are three different conditions for the surface finishing and the thickness of top-coating, t, i.e. TUC I=ground surface and t= 220 ± 20μm, TUC II=ground surface and t=400 ± 20μm, TUC III= as sprayed surface and t=250 ± 20μm. The TUCS specimens were prepared using TUC III specimens.

After blasting by white alumina (#24, air pressure of 0.4MPa), the WC-12%Co and Ni-11%P coatings were formed by high velocity flame-spraying process [2]. The chemical compositions (wt.%) of both powders are Co: 12.0, Fe: 1.0, WC: bal. for WC-12%Co and P: 11.0, C < 0.15, Ni: bal. for Ni-11%P, and the powder size is 10~45μm. The spraying distances are 150mm and 200mm for WC-12%Co and Ni-11%P respectively, and the fuel gas is C2H2 and C3H8. The Al-2%Zn coating was formed by wire metallizing process after blasting by white alumina. The chemical composition (wt.%) of the wire is Si: 0.14, Mn: 0.003, Fe: 0.18, Sn: 0.001, Mn: 0.04, Zn: 1.90, Sb: 0.0001, In: < 0.0001, Hg: < 0.0001, Al: bal. and the wire diameter is 3.2mm. The fuel gas is C2H2 and the spraying distance is 150mm. After spraying, the specimen surface was mechanically polished by diamond sheet (~#3000) for WC-12%Co and by emery paper (~#2000) for Ni-11%P and Al-2%Zn. The thicknesses of the coatings of fatigue specimens are 120 ± 30μm for WC-12%Co, 220 ± 30μm for Ni-11%P and 120 ± 20 μm for Al-2%Zn.

Experimental procedures
Fatigue tests were conducted using 98 N·m capacity rotary bending fatigue testing machines at a loading frequency of 22.7 Hz, and additional experiments for Al-2%Zn were also performed at 2.5 Hz in order to study the effect of loading frequency. The observations of crack initiation and growth behaviour were made on the longitudinal section of the specimens using an optical microscope and a scanning electron microscope (SEM).

The corrosive environment chosen is a 3%NaCl solution whose pH and dissolved oxygen content before the experiments were 7.2 and 7.82 ppm, respectively. The solution was led from a bath with 10 l capacity to the corrosion chamber through a temperature controlled bath at 30 °C and dropped to fatigue specimen at a rate of 10 cc/min. The solution was circulated between the bath and the chamber, and was renewed every 15 days.

3 Results

Electrochemical property of coatings
Before fatigue tests, the polarization curves for the metal coatings in NaCl solution were measured and shown in Fig.1. It is found that the free corrosion potential is higher for Ni-11%P and is lower for Al-2%Zn than that of the substrate steel, S45C, indicating that the former is electrochemically noble and the latter is poor against the substrate.

Fatigue strength
The S-N diagrams for sprayed steel with different coatings are represented in Fig.2; where the stress amplitude, σ_s, was calculated using only the diameter of the substrate.

The fatigue strengths of ceramic coating are almost the same as EP in air. In 3%NaCl solution, however, the fatigue strengths are considerably decreased as compared to those in air but are higher than EP (Fig.2(a)). Furthermore, TUCS exhibits almost the same corrosion fatigue strength as TUC III. These results indicate that the ceramic coating has a little effect

![Fig.1 Polarization curves for metal coatings.](image-url)
on improving the corrosion fatigue strength and the sealing treatment is ineffective at \( N_f \leq 1 \times 10^7 \) cycles.

The fatigue strength of WC-12%Co in air is significantly higher than that of EP (Fig.2(b)). The coating which has a high adhesive strength can enhance the crack initiation resistance of the substrate steel. On the other hand, the fatigue strength in 3%NaCl solution is decreased, in particular, remarkably in long life regime. However, as compared to EP, the corrosion fatigue strength is clearly improved.

As shown in Fig.2(c), the fatigue strengths of Ni-11%P in air and in 3%NaCl solution are almost identical to those of EP, indicating that the coating has no effect on fatigue strength in both environments. Cracks were observed in the coating of a specimen unbroken at \( N = 1 \times 10^7 \) cycles in air, but they did not grow successively into the substrate because of the delamination of the interface. In 3%NaCl solution, any appreciable corrosion was not seen on the surface of the coating, but some rust exuded from cracks in the coating. This suggests that a corrosion reaction had occurred at the interface between the coating and the substrate.

The fatigue strength of Al-2%Zn in air is the same as that of EP, i.e. the soft coating has no effect on the fatigue strength (Fig.2(d)). However, it should be noted that the fatigue strength in 3%NaCl solution is significantly

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**Fig. 2 S-N diagrams for sprayed steel with different coatings.** (a)Cr_2O_3, (b)WC-12%Co, (c)Ni-11%P, (d)Al-2%Zn.
Improved as high as that of the substrate in air. Furthermore, it is found that the corrosion fatigue strength is not affected by loading frequency. At 2.5 Hz, however, a remarkable corrosion dissolution was observed in the coating which peeled partially from the substrate in long life regime.

Corrosion fatigue mechanisms
As previously described, the corrosion fatigue strength of the sprayed steel depends on both the strength and the electrochemical characteristics of the coatings. In this section, the corrosion fatigue mechanisms will be discussed based on detailed observations of the longitudinal section of the specimens.

Sections are shown in Fig. 3 for the TUC III and TUCS specimens tested in 3% NaCl solution which were unbroken at $N = 1.0 \times 10^7$ cycles, where arrows indicate cracks in the substrate. In the TUC III specimen, many cracks are initiated in the substrate, which are localized near the site where a crack is observed in the top-coating. In the TUCS specimen, no cracks can be seen in the substrate. Although there was no significant difference in fatigue life between the TUC III and TUCS specimens (Fig. 2(a)), Fig. 3 suggests that the sealing treatment would improve corrosion fatigue strength in longer life regime of $N > 1 \times 10^7$ cycles.

The sections of a WC-12%Co specimen which was broken at fatigue life, $N_f = 1.2 \times 10^7$ cycles, are presented in Fig. 4. The coating peeled from the specimen surface over a few millimeter long. Figure 4(a) shows the region where the coating completely peeled and (b) the region where it still attached to the surface. It can be seen in Fig. 4(a) that there are many cracks which initiate from corrosion pits generated at the substrate. Cracks are also observed in the substrate to which the coating attached, but no
crackings exist in the coating (Fig. 4(b)). It was also established that any cracking was not seen on a specimen stressed to 90% of $N_f$.

Figure 5 reveals the section of a Ni-11%P specimen which was broken at $N_f = 3.4 \times 10^6$ cycles. This coating has very low resistance to cracking under cyclic stress. As can be seen from the figure, there exists a crack in the coating. The crack changes the growth direction to the direction along the interface, i.e. the crack does not grow continuously into the substrate because of the delamination of the interface. The volume fraction of pores is relatively low in the coating, but the solution can be supplied to the substrate through such cracks, then leading to the generation of corrosion pits and crack growth in the substrate. Consequently, the improvement of corrosion fatigue strength cannot be expected by spraying Ni-11%P.

Figure 6 shows the section of a Al-2%Zn specimen which was unbroken at $N = 1.0 \times 10^7$ cycles. The coating has a large volume fraction of pores of approximately 10%. Thus, the solution is easily supplied to the interface through pores. Since the coating is electrochemically poor against the substrate, the anodic dissolution takes place in the coating and the substrate is in the state of cathodic protection. Any corrosion pits and cracks are not observed in the substrate as shown in the figure. Therefore, the corrosion fatigue strength was improved dramatically up to the strength of the sub-
strate in air. On the other hand, the anodic dissolution of the coating begins at the interface and proceeds to the inside of the coating. Consequently, the coating is filled up with corrosion products whose strength is very low, thus the coating can peel easily. As shown in Fig. 2(d), the corrosion fatigue strength at 22.7Hz was almost the same as that at 2.5Hz in the region of $N \leq 1 \times 10^7$ cycles. However, in much longer life regime or at lower loading frequencies, the corrosion dissolution of the coating would take place much more severely and thus the coating would peel from the substrate. If it peels completely, then the corrosion fatigue strength would be the same as that of EP.

4 Discussion

In ceramic coating, the solution can trace pores in the coating and is supplied to the interface. Subsequently, local cells are formed at the interface and cause the initiation of corrosion pits. The corrosion in the interface assists the delamination of the interface, thus the solution can be supplied to surrounding region. By sealing, the solution is supplied only from cracks in the coating, thereby contributing to an improved corrosion fatigue strength in the longer life regime where no crack is initiated. When the applied stress is increased, many cracks are initiated in the coating and thus a plenty of the solution is supplied to the interface. Therefore, the effect of the sealing disappears in the region of $N \leq 1 \times 10^7$ cycles. The WC-12%Co specimens indicate similar corrosion fatigue process to ceramic-coated specimens. However, the coating has a high resistance to cracking and a good sealing effect [3], thus the improved corrosion fatigue strength can be obtained.

The Ni-11%P coating has a poor resistance to cracking under cyclic stress and a low adhesive strength, thus corrosive media is easily supplied to the substrate through cracks, leading to no improvement of corrosion fatigue strength. In metal coatings, a method in which coating is used as a sacrifice electrode is considered to be very effective as shown for the Al-2%Zn coating. However, it should be noted that the effectiveness would be lost if the coating peels completely.
Finally, in order to improve the corrosion fatigue strength, it is necessary to use the coatings which have a good resistance to cracking and high adhesive strength, and also to seal many pores inevitably contained in sprayed coatings.

5 Conclusions

In the present study, in order to investigate fatigue strength of sprayed steel, rotary bending fatigue tests were conducted at room temperature in air and in 3%NaCl solution. A medium carbon steel (S45C) sprayed different coatings of a ceramic (Cr_2O_3), a cermet (WC-12%Co) and metals (Ni-11%P and Al-2%Zn) was used as test specimens. The results obtained were summarized as follows;

(1) The corrosion fatigue strength was slightly improved by ceramic-sprayed coating. A sealing treatment was effective when the fatigue life was longer than $1 \times 10^7$ cycles, while it had little effect on improving the corrosion fatigue strength when many cracks were initiated in the coating.

(2) The corrosion fatigue strength of WC-12%Co was improved as compared to that of the substrate steel, because of the good sealing effect of the coating. However, since the corrosive media could be supplied from the specimen surface to the substrate through pores contained in the coating, fatigue failure took place by the initiation of corrosion pits and subsequent crack growth.

(3) For Ni-11%P, cracks were initiated easily in the coating at the extremely early stages of fatigue cycling. Therefore, the corrosion fatigue strength was the same as that of the substrate steel, because the corrosive media could easily be supplied to the substrate through cracks and pores.

(4) The anodic dissolution took place in the Al-2%Zn coating and no corrosion occurred in the substrate, because the coating was electrochemically poor against the substrate steel. Consequently, the corrosion fatigue strength was improved as high as that of the substrate in air.

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References

