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Effects of yttrium and cerium additives in lubricants on corrosive wear of stainless steel 304 and Al alloy 6061

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Effects of oxygen active elements, yttrium and cerium, as additives in commercial lubricants on corrosive wear were investigated. Sliding wear losses of stainless steel 304 and Al alloy 6061 lubricated by oil and thin grease respectively with and without yttrium or cerium additive in a corrosive environment were determined. Dilute H_2SO_4 solution (10% H_2SO_4) was used as the corrosive medium and added to the lubricants for the corrosive wear test. The wear test was performed on a pin-on-disc tribometer with the capability of measuring wear in lubricant. The disc was coiled with a copper tube, through which cooling water could pass, so that the wear losses respectively under cooling condition and non-cooling condition could be determined. The results showed that wear losses of the tested materials caused by synergistic attack of wear and corrosion can be effectively reduced by adding small amounts of yttrium or cerium to the lubricant. In addition, the effect of the additives was found more distinctive under the non-cooling condition. Worn surfaces were examined using SEM to clarify the wear mode and thus the wear mechanism. © *2000 Kluwer Academic Publishers*

1. Introduction

Corrosive wear often results in severe material losses. Since this wear mode is common in mining, mineral and chemical processing, energy production industries as well, the synergic attack by wear and corrosion has received increasing interest [1, 2]. Efforts are being made to develop effective techniques to diminish corrosive wear of materials. Previous research and engineering efforts in combating corrosive wear include modification of existing materials, surface protection, and environmental control. However, no general approaches have been developed to efficiently prevent corrosive wear.

In general, guidelines for selecting or modifying engineering materials against either corrosion or wear have been well established. Adequate materials can be reasonably selected or developed to resist mechanical wear such as abrasive wear in the absence of electrochemical reactions. This may be achieved, for instance, by increasing the hardness of the material through precipitation strengthening or embedding hard particles into the matrix to form wear-resistant composites. However, such fabricated materials are not necessarily suitable for corrosive wear applications because the materials may have a low corrosion resistance due to the microstructural inhomogeneity. In the case of corrosion, the material degradation can be reduced by alloying with elements, e.g., Cr or Al, which assist in preventing corrosion attack by forming a protective oxide film, Cr_2O_3 or Al_2O_3. It is known that the corrosion resistance of a corrosion-resistant material may result from the rapid passivation with forming a protective oxide film on the surface [3, 4]. However, when wear is involved, the protective oxide film can be broken down and removed from the surface. The resultant bare metal surface is vulnerable to continuous corrosion-wear attack. Furthermore, the residual fragements of the oxide film on the surface may act as the cathodes and thus accelerate the corrosion process. The combined effect of wear and corrosion can make corrosion-resistant materials such as stainless steels as ineffective as ordinary carbon steels to such attack.

An attempt has been made by the present authors to combat corrosive wear by using oxygen-active elements, e.g., yttrium and cerium, as additives in lubricant. Recent work reported by Zhang and Li [5, 6] have demonstrated that oxygen-active elements can considerably enhance the resistance of stainless steel and aluminide coatings to corrosive wear as well as to corrosion. They observed that the polarization behavior of 304 stainless steel was greatly improved when it contained 1 wt %Y and also the volume loss of the Y-containing 304 steel in corrosive wear was markedly lower than that of 304 steel. In addition, they did not observe significant influence of yttrium on the mechanical properties of 304 steel. This implies that the role of yttrium in improving the corrosive wear resistance is not to enhance the mechanical behavior of the steel but to enhance its corrosion resistance. It is known that inhibiting corrosion can decrease the synergistic action of corrosion and wear, and thus diminish the corrosive wear. Although it is clear that the reduction in corrosive wear by alloying yttrium is mainly attributable to the inhibition of corrosion, the mechanism responsible for the reduction in corrosive wear is still not understood well on finer levels. Another possible effect of yttrium is the enhancement of the oxide adherence. In a corrosive environment, stainless steel can rapidly form a protective oxide film on the surface to prevent further corrosion. However, the breakdown of the film under the combined attack by wear and corrosion makes the stainless steel ineffective. If the bonding between the oxide film and the substrate is enhanced, the protective role of the oxide film could be improved. Oxygen-active elements may strengthen the interfacial bonding. Previous studies on oxidation of Al and Cr alloys [7–22] show that the bonding between the oxide films and the alloys can be significantly enhanced by alloying with small amounts of oxygen active elements. Although these studies are focused on the effect of oxygen-active elements on the oxide films developed during oxidation, it is also possible that the oxygen-active elements may play a similar role in enhancing the oxide adherence during corrosion. However, this is just a hypothesis and the conclusion can not be drawn without justification. The mechanism responsible for the beneficial effect of oxygen-active elements could be the improvement in polarization behavior; this enhances the corrosion resistance, thus leading to an increase in the resistance to corrosive wear. Polarization tests [5] have demonstrated that the passivation current of 304 steel can be considerably reduced by alloying with small amounts of yttrium, and such a reduction was also observed when yttrium was added to aluminide coatings, alone with an increase in the corrosion potential [6]. The improved polarization behavior is definitely beneficial to decreasing the synergy of corrosion and wear.

Although the mechanism responsible for the reduction in corrosive wear by alloying with oxygen-active elements are not completely understood, the beneficial effect of the elements on inhibiting corrosive wear has been experimentally confirmed. In this study, an attempt was made to reduce corrosive wear of stainless steel and aluminum alloy by adding small amounts of fine yttrium and cerium powder to lubricants. It was anticipated that, the yttrium and cerium additives could function similarly to that when they were alloyed into the materials. The practical significance of this research lies in improving commercial grease lubricants using the oxygen active additives for corrosion-wear applications.

2. Experimental details

Wear tests were performed on a pin-on-disc tribometer. The tested materials were stainless steel 304 and aluminum alloy 6061. The chemical compositions and mechanical properties of the materials are listed in Tables I and II, respectively. The dimensions of the pin specimens for the wear testing were 6 × 12 × 40 (mm). The surface of the specimens was flat so that the nominal contact pressure could remain constant. The specimens were machined from commercial stainless steel and aluminum alloy bars. The surface of the specimens was smoothly finished by a lathe, with an average roughness (Ra) equal to 1.0 μm. The disc was made of stainless steel 304. The roughness (Ra) of the disc surface was 2.5 μm. The disc was set into a container which has a wall of 10 mm high to retain the lubricant. A coil of copper tube was attached to the bottom of the container, through which cooling water could pass to reduce the temperature rise caused by frictional heat.

TABLE I Chemical compositions

SS 304	C	Mn	P	S	Si	Cr	Ni		
	0.08	2.0	0.04	0.03	1.0	19.0	9.0		
Al 6061	Cu	Si	Fe	Mn	Mg	Zn	Cr	Ti	Al
	0.3	0.6	0.7	0.15	1.0	0.25	0.2	0.15	Balance

TABLE II Mechanical properties

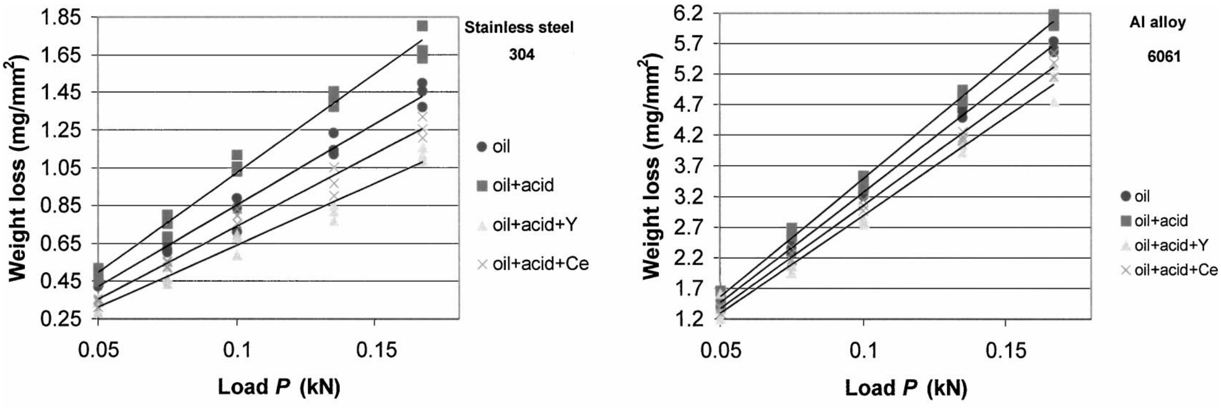
Mechanical properties/ Materials	Tensile strength (MPa)	Yield strength (MPa)	Elongation (% in 50 mm)	Brinell hardness
SS 304	579	276	50	200
Al 6061	238	154	21	65

A vegetable-based oil lubricant and polyester grease were used for the wear test. The former did not contain petroleum or mineral components and heavy metals; the latter was non-metallic and non-silicone. Small amounts (less than 5 vol.%) of yttrium powder (420 micron, 99.9%) and cerium powder (250 micron, 99.9%) were added to the lubricants, respectively. In order to evaluate the wear performance of the tested materials in a corrosive environment, 10% H_2SO_4 was added to the lubricants with the volume ratio of H_2SO_4 to, for example, the oil lubricant approximately equal to 1 : 4. For a comparison, wear tests were conducted in plain oil, oil-H_2SO_4, oil-H_2SO_4-Y and oil-H_2SO_4-Ce lubricants, respectively. The sliding speed was 60 m/min. The wear resistance of the material was evaluated by measuring its weight loss after sliding over 600 m. In order to investigate the effect of normal load on the wear loss, the applied load P was changed in the range from 0.05 to 0.167 kN, corresponding to a contact pressure from 0.7 to 2.3 MPa. To reflect the effects of temperature rise caused by frictional heat on corrosive wear, the wear tests were conducted under cooling and non-cooling conditions, respectively.

3. Results and discussion

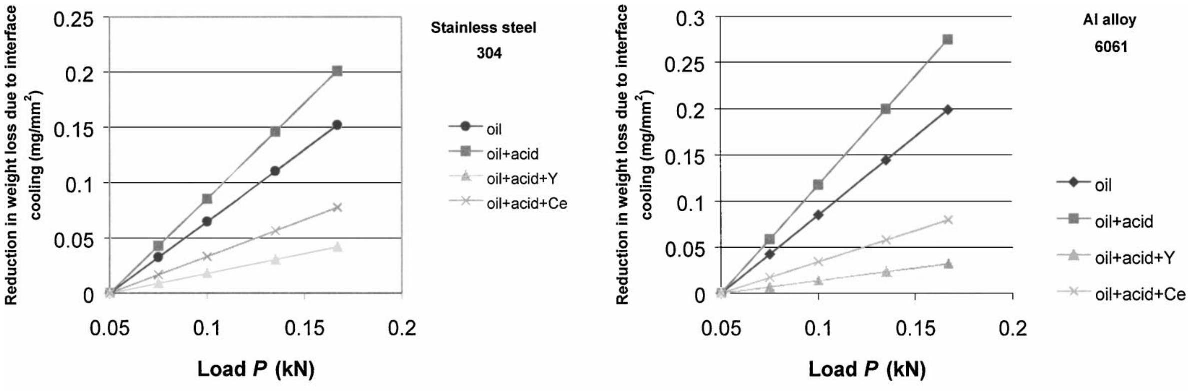
3.1. Wear losses

Weight losses of stainless steel 304 and the aluminum alloy 6061 per unit contact area were measured, with respect to the applied load. Wear under four lubrication conditions was investigated, i.e. in plain oil, oil-H_2SO_4, oil-H_2SO_4-Y and oil-H_2SO_4-Ce lubricants, respectively. Fig. 1a and b illustrate the results of wear losses without cooling. Under each load, three specimens were tested in the same condition and linearized



(a) (b)

Figure 1 Wear losses under non-cooling condition vs. the applied load; (a) Stainless steel 304, (b) aluminum alloy 6061.



(a) (b)

Figure 2 Reductions in wear loss, caused by cooling the disc, vs. the applied load; (a) Stainless steel 304, (b) aluminum alloy 6061.

weight loss ~ load curves were obtained using the least-square method. It was observed that corrosive wear under the oil-H_2SO_4 lubrication condition resulted in the largest weight loss, while wear in plain oil resulted in less weight loss. However, when the wear test was performed in the oil-H_2SO_4-Y or the oil-H_2SO_4-Ce lubrication condition, the corrosive wear was markedly reduced and the resultant weight losses were even smaller than that under the plain oil lubrication condition. Also, yttrium showed a greater effect than cerium on inhibiting corrosive wear. It should be mentioned that the presented results were obtained in liquid lubricant, i.e. oil, but no distinct difference was observed when thin grease was applied, in which the Y or Ce powder was distributed homogeneously. Under the maximum load of 167 kN, the combined attack by corrosion and wear increased the wear of the stainless steel by a factor about 21%, and that of the aluminum alloy by a factor of about 7%. When yttrium or cerium was added to the lubricant, the wear losses of both the stainless steel and the aluminum alloy were markedly reduced; the differences became more obvious with increase in applied load. This is clearly shown in Fig. 1a, which illustrates the wear losses of stainless steel 304 under different lubrication conditions. 38% and 29% reductions in corrosive wear of the stainless steel were observed when Y and Ce respectively were added to the lubricant, while 17% and 12% reductions were observed for Al alloy 6061, under the maximum load of 167 kN.

In addition, it was found that the wear loss was considerably reduced when the disc or the counterface was cooled. In order to investigate the cooling effect, differences between the wear loss under the cooling condition and that under non-cooling condition were determined. The reductions in wear loss of stainless steel 304 and Al alloy 6061 caused by cooling the disc are illustrated in Fig. 2a and b, respectively. In the plain oil lubrication condition, when the disc was cooled, the wear loss was greatly reduced and the reduction was more significant under high loads. This phenomenon is understandable, based on the fact that frictional heat may increase the extent of adhesive wear and/or corrosive wear. They became more severe as the applied normal load was increased, because the friction increased with the applied load. When corrosion was involved by adding H_2SO_4 to the oil, the situation became even worse. This occurred because the temperature rise due to friction also accelerated the corrosive reaction and, thus, resulted in greater corrosive wear loss. In this case, the cooling effect on the reduction in wear loss was greater. However, it may be seen in Fig. 2 that, when yttrium or cerium additive was used, the cooling effect on the reduction in corrosive wear was not as large as that without the additives. This implies that yttrium and cerium effectively reduced the negative effect of the friction heat on corrosive wear, thus decreasing the difference between the wear under the cooling condition and that under the non-cooling condition. In other words, the oxygen-active additives were more effective at elevated temperatures. Therefore, it can be concluded that yttrium and cerium additives played a more distinctive role in reducing corrosive wear in the case of corrosion and adhesion were promoted due to greater friction heating under higher loads.

3.2. SEM analyses of worn surfaces

In order to understand better the protective effect of Y and Ce additives on corrosive wear, worn surfaces of stainless steel 304 and Al alloy 6061 were examined using SEM. The damage by corrosion and mechanical wear is clearly illustrated in Figs 3–7. During a wear process, plough indents were formed on the material surface due to the mechanical force. The edges of the plough indents are the areas with large plastic deformation, associated with a high density of dislocations. Since the intensely deformed regions become anodes and the other regions are the cathodes in a corrosive environment [1], they are with high activity for corrosion. Therefore, wear expedites the electrochemical reaction and promotes the material removal thereby [23, 24]. On the other hand, the density of defects, such as dislocations and voids, is high in the plastically deformed

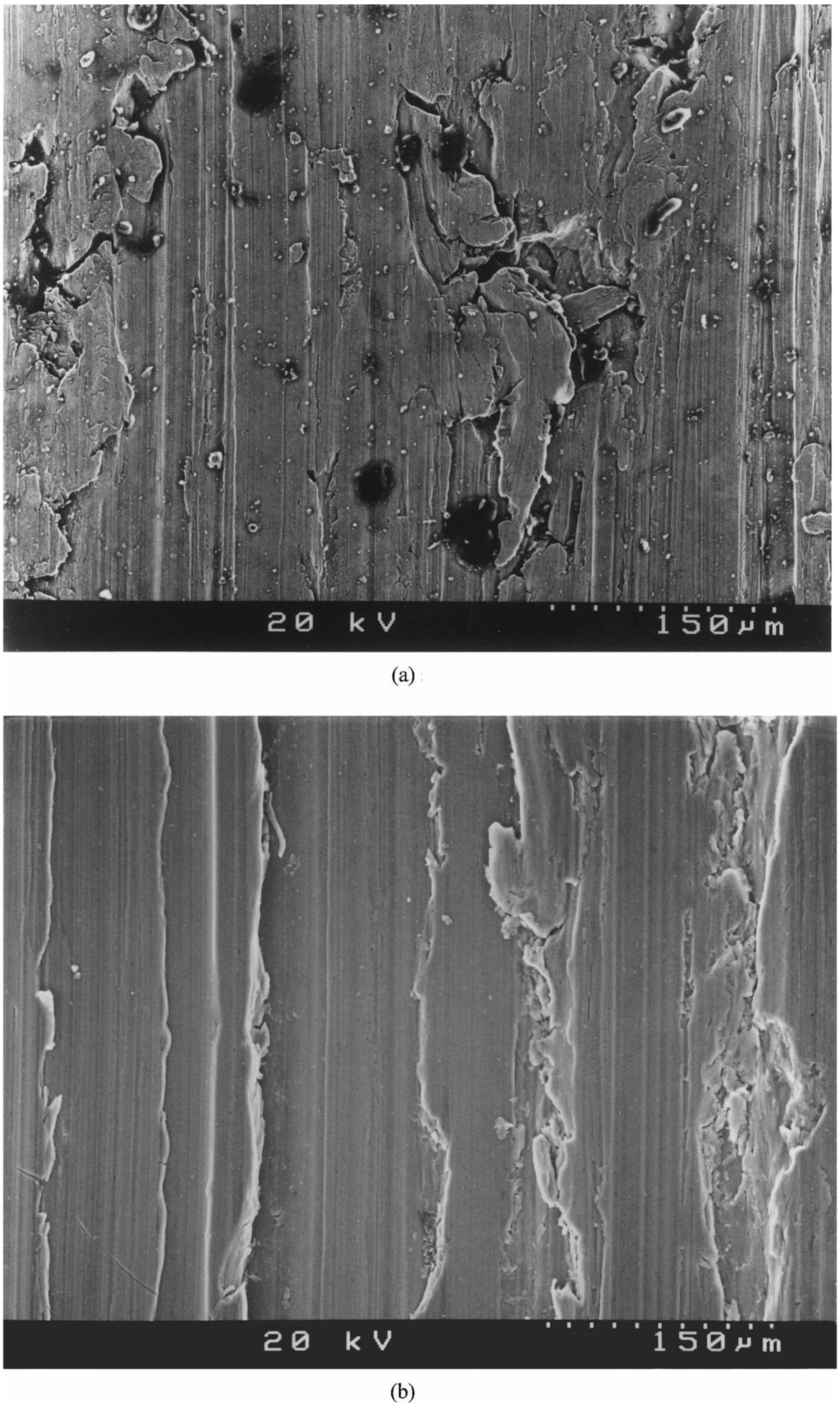
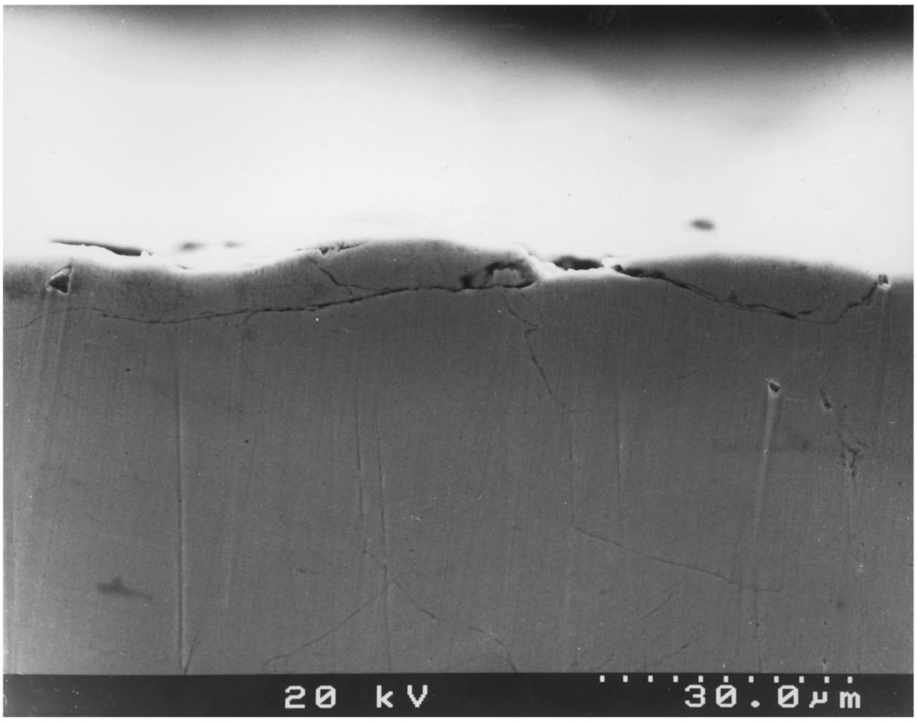
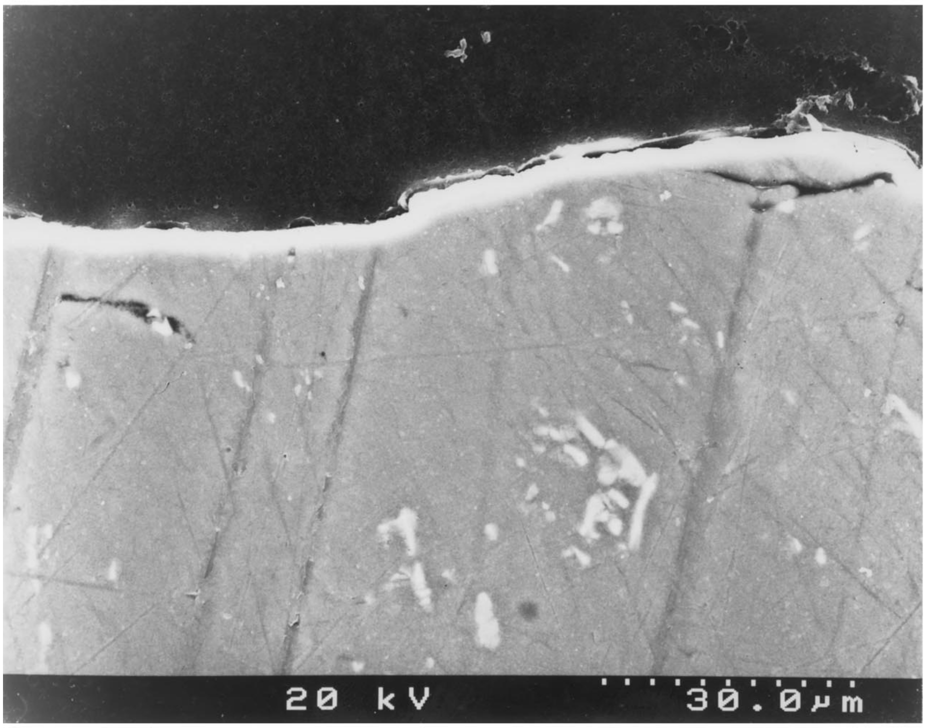


Figure 3 SEM micrographs of worn surfaces under oil-H_2SO_4 lubrication condition; (a) Stainless steel 304, (b) aluminum alloy 6061.



(a)

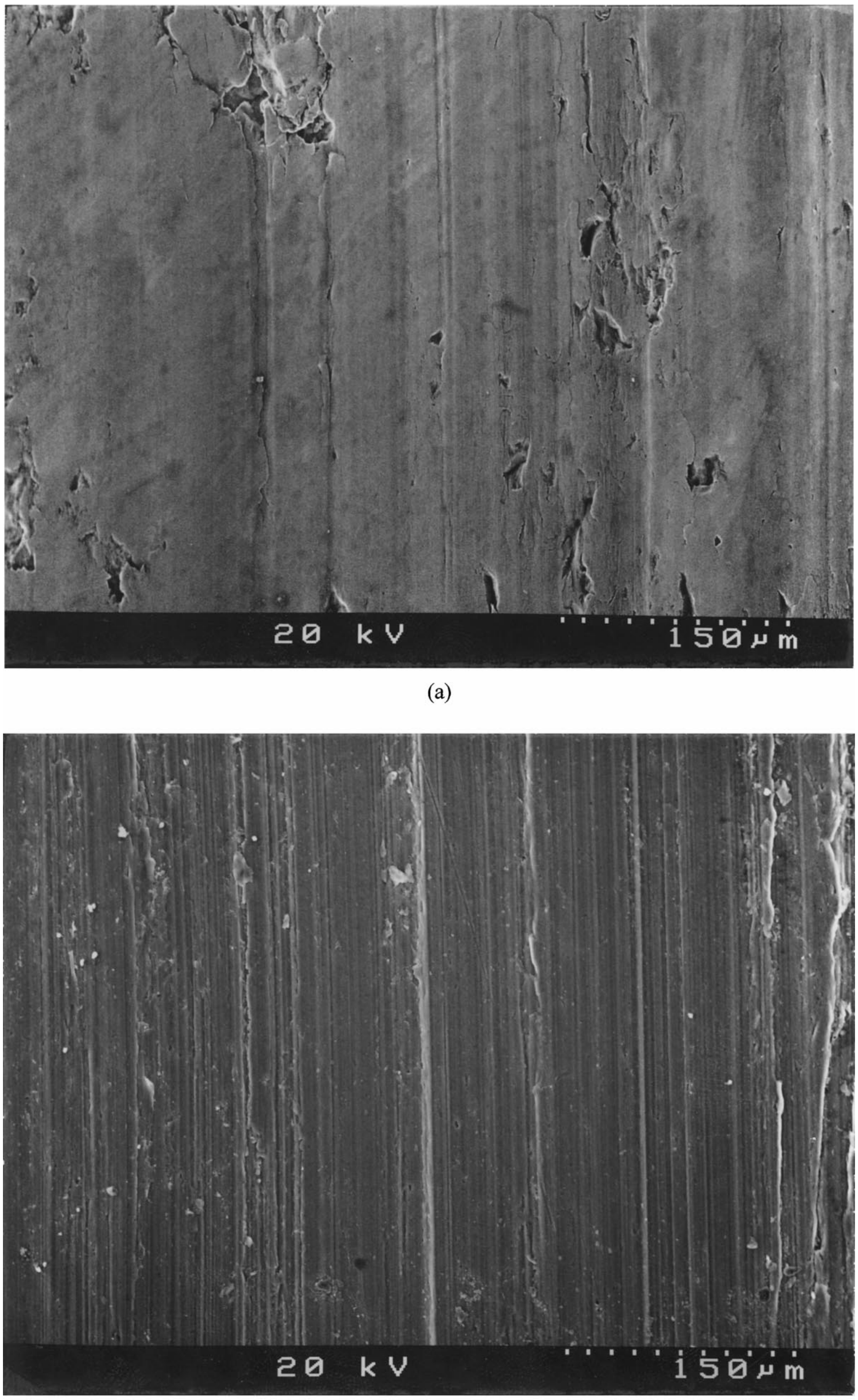


(b)

Figure 4 SEM micrographs of the cross section of the worn surfaces shown in Fig 3; (a) Stainless steel 304, (b) aluminum alloy 6061.

regions; as a result, these regions are relatively easy for the corrosive medium to penetrate, which may promote cracking when corrosion and stress simultaneously attack the surface. As shown in Fig. 3, cracks of various lengths and depths exist in the corroded regions. With the propagation of initiated cracks under an external force, the cracks eventually propagated to form deep fractures, which can be clearly seen in the cross-section metallographs of the surface layer (see Fig. 4). Since the propagation of cracks due to the simultaneous corrosion and stress attacks is more rapid than crack propagation under mechanical wear, the extent of material removal by corrosive wear is more severe.

A significant improvement in the reduction of cracking by yttrium and cerium additives during corrosive wear was observed (see Fig. 5). Compared to the cracked and fractured surfaces without Y or Ce protection, shown in Fig. 4, few cracks are found in the surface layers when Y or Ce additive was added to the lubricant (see Fig. 6). This elimination of cracking by



(a)

(b)

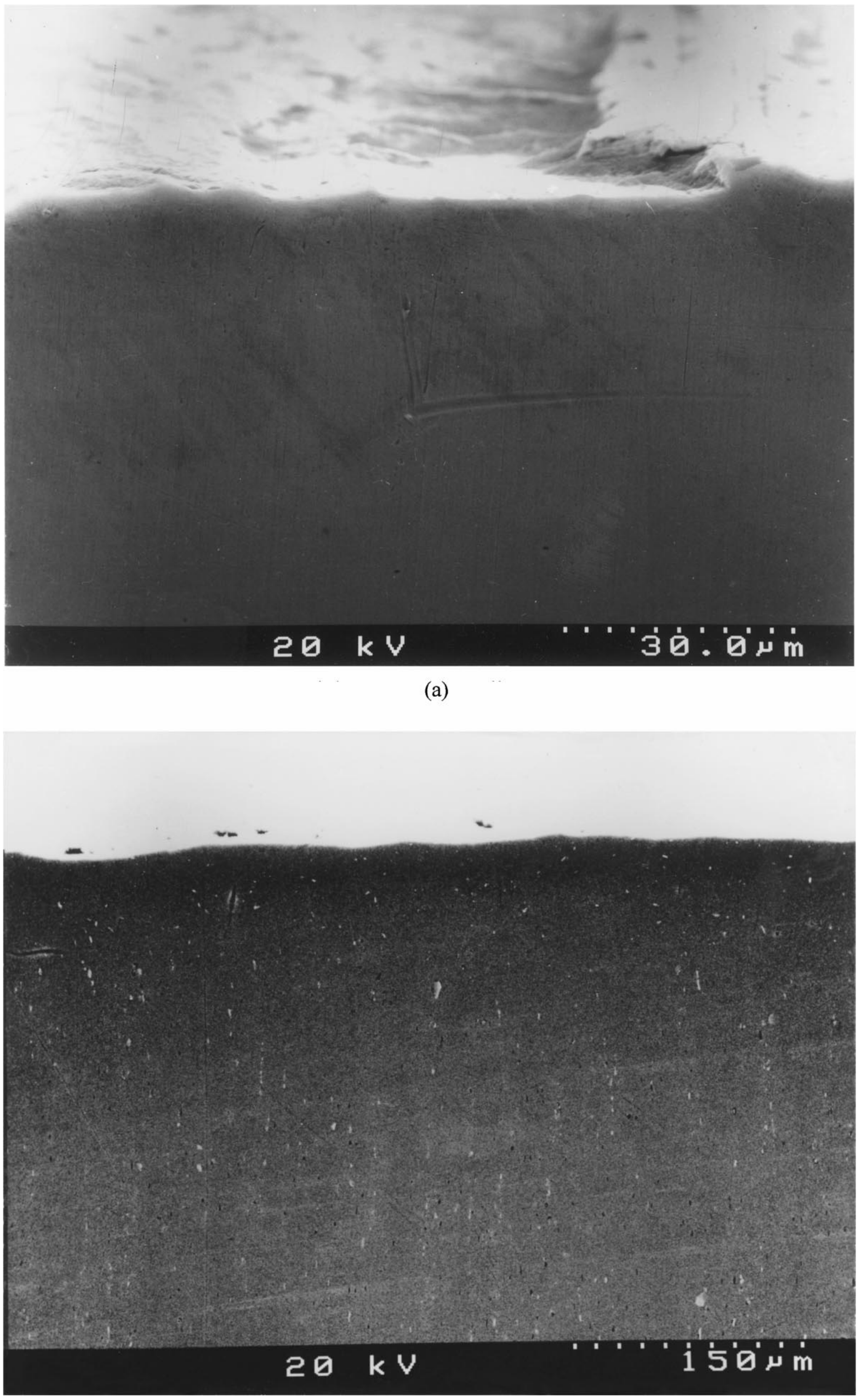
Figure 5 SEM micrographs of worn surfaces under oil-H_2SO_4-Y (or Ce) lubrication condition; (a) Stainless steel 304 in oil-H_2SO_4-Y, (b) aluminum alloy 6061 in oil-H_2SO_4-Ce.

yttrium or cerium is consistent with the results of the sliding wear tests.

In regard to the worn surfaces in the plain oil, plastic flow was observed in most regions of the surface, see Fig. 7a, and cracks were found below the surface in the cross-section of the specimen, see Fig. 7b. It is known that the sliding wear of a material in non-corrosive conditions depends on its mechanical properties, the applied load, and the contact geometry. The subsurface of the material undergoes plastic deformation. When the maximum plastic strain beneath the contact area accumulates and reaches the fracture strain of the material, cracks nucleate, then propagate, and eventually lead to material delamination at the surface [23–25]. Furthermore, direct rubbing between two surfaces may increase the adhesive force due to the frictional heat. When a high load is applied, the temperature at the counter-face increases. As a result of the increase in adhesion, the contact surfaces tend to stick to each other, which enhances material transfer or removal from the surface in bulk, as shown in Fig. 7a.

3.3. Discussion on corrosive wear and the beneficial effect of yttrium and cerium

The wear tests and the SEM analysis of worn surfaces showed that the presence of yttrium or cerium in



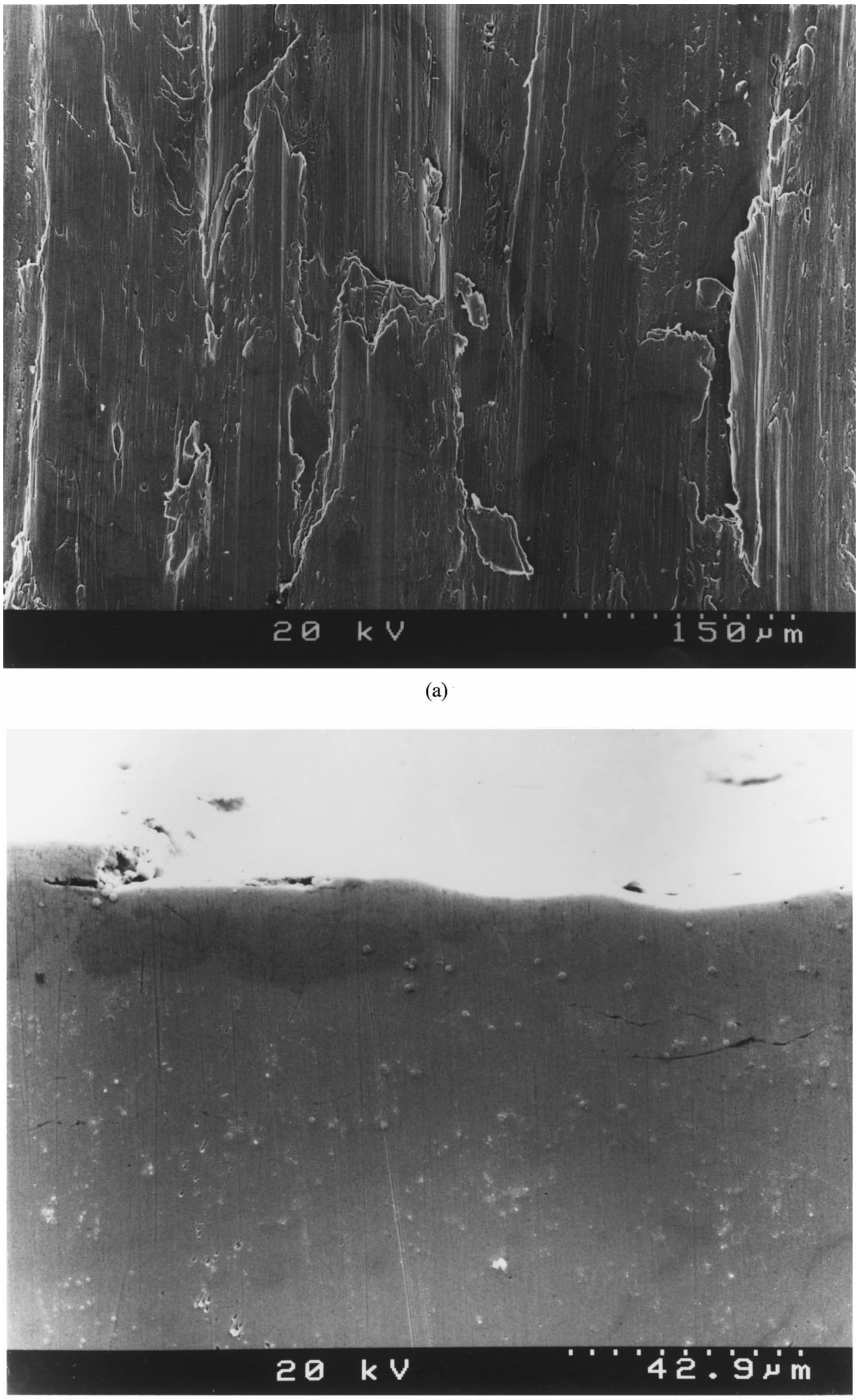
(a)

(b)

Figure 6 SEM micrographs of the cross section of the worn surfaces shown in Fig. 5. (a) Stainless steel 304 in oil-H_2SO_4-Y, (b) aluminum alloy 6061 in oil-H_2SO_4-Ce.

lubricant as an additive markedly diminished the corrosive wear of stainless steel 304 and Al alloy 6061 in dilute H_2SO_4 solution. Corrosion of a metal usually produces loose and fragile oxide scales. The higher the temperature of the corrosive medium, the more rapid is the electrochemical reaction, leading to aggravated corrosion damage. Corrosive wear is an action combining mechanical wear and electrochemical reaction and these two factors can enhance each other. During corrosive wear, both anodic and cathodic reactions occur. According to electrochemical theory [26, 27], defects in a metal, such as dislocations, grain boundaries, and precipitates, are relatively anodic to the rest of the material, and the corrosion penetrates selectively along these defects. Various defects generated by wear, therefore, promote the corrosion process. On the other hand, corrosion can accelerate the material removal by wear, e.g., stress-corrosion cracking is one of well-known combined effects of corrosion and stress. Therefore, if either corrosion or mechanical wear is suppressed, the corrosive wear could be greatly diminished.

Regarding the role of yttrium and cerium playing in corrosive wear, it appears that they mainly help to inhibit corrosion, as little influence of these elements on the mechanical behavior of the materials was observed [5, 6]. The polarization measurement by Zhang



(a)

(b)

Figure 7 SEM micrographs of worn stainless steel 304 in plain oil. (a) Worn surface, (b) cross section.

and Li [5, 6] provides direct evidence that the oxygen-active elements can strongly improve the polarization behavior of stainless steel and aluminide coatings. An improved corrosion resistance definitely benefits the reduction in corrosive wear because the synergy of corrosion and wear can be weakened if the corrosion process is suppressed. The effect of oxygen-active elements on inhibiting corrosion was also reported by other researchers. For instance, Lu and Ives [28] demonstrated that cerium implantation into UNS S31603 stainless steel effectively inhibited the cathodic kinetics of the reduction of oxygen and protons in a solution, reducing the rate by more than two orders of magnitude. The passive current density during anodic polarization was reduced by more than one order of magnitude after cerium implantation, indicating that cerium affected the anodic reaction kinetics as well. The cerium implantation, as they discussed, helped to reduce the cathodic and anodic reactivities by blocking the reactive surface sites, such as kinks in atomic ledges.

It should be noticed that it is not very clear how yttrium and cerium affect the corrosion and thus corrosive wear on finer levels, but the beneficial effect of Y and Ce might be attributable to 1) possible improvement in the interfacial bonding between the oxide film and the substrate, 2) corresponding microstructural changes of the oxide, and 3) possible improvement in the self-healing capability of the adherence. Further studies are needed in order to justify the above possible mechanisms.

It was interesting to observe that the weight loss under the oil-H_2SO_4-Y lubrication condition was surprisedly lower than that in the plain oil, as shown in Fig. 1. It is possible that yttrium or cerium in the lubricant may act as interfacial separators to reduce the adhesion between two sliding metal surfaces and thus cracking and adhesive wear. However, it should be indicated that it is unclear how yttrium or cerium powder in lubricant interacted with the sliding surfaces and how it influenced the corrosion process, since in lubricant Y and Ce may act differently from the case when they are in alloying state. Further investigation on this issue is necessary.

4. Conclusions

Effects of oxygen active elements, yttrium and cerium, as additives in lubricants on corrosive wear of stainless steel 304 and aluminum alloy 6061 were investigated. It was demonstrated that the yttrium and cerium additives markedly reduced corrosive wear of the tested materials. The beneficial effect of the oxygen active elements on corrosive wear could be attributable to their effect on inhibiting corrosion, which reduced the synergy of corrosion and wear. The mechanisms responsible for the reduction in corrosive wear by Y and Ce were discussed.

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References

1. B. W. MADSEN, "ASM Handbook: Friction, Lubrication, and Wear Technology," Vol. 18 (Bureau of Mines, USA, 1998) pp. 271–277.
2. A. V. LEVY, "Solid Particle Erosion and Erosion-Corrosion of Materials" (ASM International, Materials Park, Ohio, USA 1995).
3. R. J. McKAY and R. WORTHINGTON, "Corrosion Resistance of Metal and Alloys" (New York, USA, 1946).
4. U. R. EVANS, "The Corrosion and Oxidation of Metals," Second Supplementary Volume (Edward Arnold, London, 1976).
5. T. C. ZHANG and D. Y. LI, *Mater. Sci. & Tech.* to be published.
6. *Idem.*, *Surface & Coatings Technology*, to be published.
7. E. J. FELTEN, *J. Electrochem. Soc.* **108** (1961) 490–495.
8. C. S. WUKUSICK and J. F. COLLINS, *Mat. Res. And Standards* **4** (1964) 637–646.
9. J. M. FRANCIS and W. H. WHITLOW, *Corrosion Science* **5** (1965) 701–710.
10. J. K. TIEN and F. S. PETTIT, *Metallurgical Transactions* **3** (1972) 1587–1599.
11. F. CLEMENDOT, J. M. GRAS, J. C. VAN DUYSEN and G. ZACHARIE, *Corrosion Science* **35** (1993) 901–908.
12. B. A. PINT, *Oxidation of Metals* **45** (1996) 1–37.
13. A. U. SEYBOLT, *Corrosion Science* **6** (1966) 263–269.
14. C. S. GIGGINS, E. J. FELTEN and F. S. PETTIT, in "Stress Effects and the Oxidation of Metals," Materials Science Symposium, edited by J. V. Cathcart (Metallurgical Society of AIME, New York, 1975) pp. 245–261.
15. T. A. RAMANARAYANAN and R. PETKOVIC-LUTON, *Oxidation of Metals* **29** (1988) 445–472.
16. W. E. KING, J. H. PARK, J. L. ROUTBORT and K. C. GORETTA, *ibid.* **29** (1988) 217–223.
17. J. E. ANTILL, M. J. BENNETT, R. F. A. CARNEY, G. DEARNALEY, F. H. FERN, P. D. GOODE, B. L. MYATT, J. F. TURNER and J. B. WARBURTON, *Corrosion Science* **16** (1976) 729–745.
18. J. C. PIVIN, C. ROQUES-CARMES, J. CHAUMONT and H. BERNAS, *ibid.* **20** (1980) 947–962.
19. M. J. CRISTOBAL, P. N. GIBSON and M. F. STROOSNIJDER, *ibid.* **38** (1996) 805–822.
20. K. Y. KIM, S. H. KIM, K. W. KWON and L. H. KIM, *Oxidation of Metals* **41** (1994) 179–201.
21. Y. LONGA and M. TAKEMOTO, *ibid.* **41** (1994) 301–321.
22. S. ROURE, F. CZERWINSKI and A. PETRIC, *ibid.* **42** (1994) 75–102.
23. M. F. ASHBY and D. R. H. JONES, "Engineering Materials 1, An Introduction to Their Properties and Applications" (Bodmin, Cornwall, 1980) pp. 241–249.
24. F. A. A. CRANE and J. A. CHARLES, in "Selection and Use of Engineering Materials" (Letchworth, Herts, 1984) pp. 178–183.
25. N. P. SUH, "Tribophysics" (Englewood Cliff, New Jersey, 1986) pp. 195–221.
26. R. H. JONES and R. E. RICKER, in "Stress-Corrosion Cracking, Materials Performance and Evaluation," edited by R. H. Jones (Ohio, USA, 1992) pp. 1–40.
27. H. KAESCHE, "Metallic Corrosion, Principles of Physical Chemistry and Current Problems" (Houston, Texas, 1985).
28. Y. C. LU and M. B. IVES, *Corrosion Science* **34** (1993) 1773–1785.

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